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On a New Mechanism of S–O Scission in the Solvolysis of Aryl Triflates*

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The solvolysis of 3,3-di-*tert*-butyl-4-hydroxyphenyl triflate (**7**) in trifluoroethanol buffered with the non-nucleophilic base, 2,6-di-*tert*-butyl-4-methylpyridine proceeds surprisingly fast. This phenomenon is explained by a new type of elimination of triflinate anion from the conjugate base **10** of the triflate **7** to form 2,6-di-*tert*-butyl-1,4-benzoquinone.

INTRODUCTION

The chemistry of vinyl triflates (**1**) has been extensively investigated in understanding vinyl cations **2** or unsaturated carbenes **3**, where the excellent leaving ability of the triflate group has played an important role to generate such reactive intermediates[1] (Scheme 1).

On the other hand, the chemistry of aryl triflates **4** has been little explored although a large number of aryl triflates have been prepared. Generally different from vinyl triflates, aryl triflates are highly stable and several attempts to generate aryl cations **5** from aryl triflates in solvolysis have proved unsuccessful.[2] The aryl triflates

* Dedicated to Professor Dionis E. Sunko on the occasion of his seventieth birthday.
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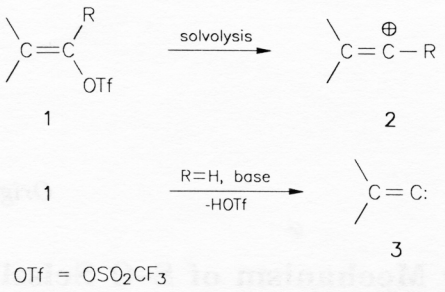
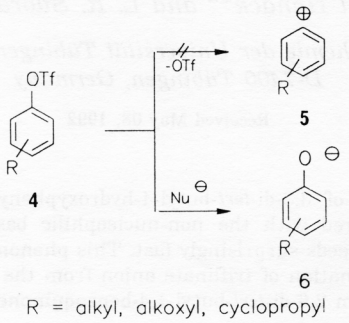


Scheme 1

were recovered unchanged in polar but non-nucleophilic solvents even after heating at 150–200 °C for several days.[2d] The only exception is the solvolysis of *o*-trimethylsilyl substituted aryl triflates in trifluoroethanol at 120 °C, which is shown to take place *via* α,β-silicium stabilized aryl cations.[3]

Under nucleophilic conditions, however, preferential nucleophilic attack at sulfur atom of the triflate group has always resulted in S–O bond cleavage to give aryloxy anions **6** (Scheme 2). These attempts have confirmed the high energy of aryl cations **5**, in which a vacant sp^2 orbital of the singlet aryl cations cannot be inherently stabilized by direct conjugation with π-donating substituents as in vinyl cations.[1]



Scheme 2

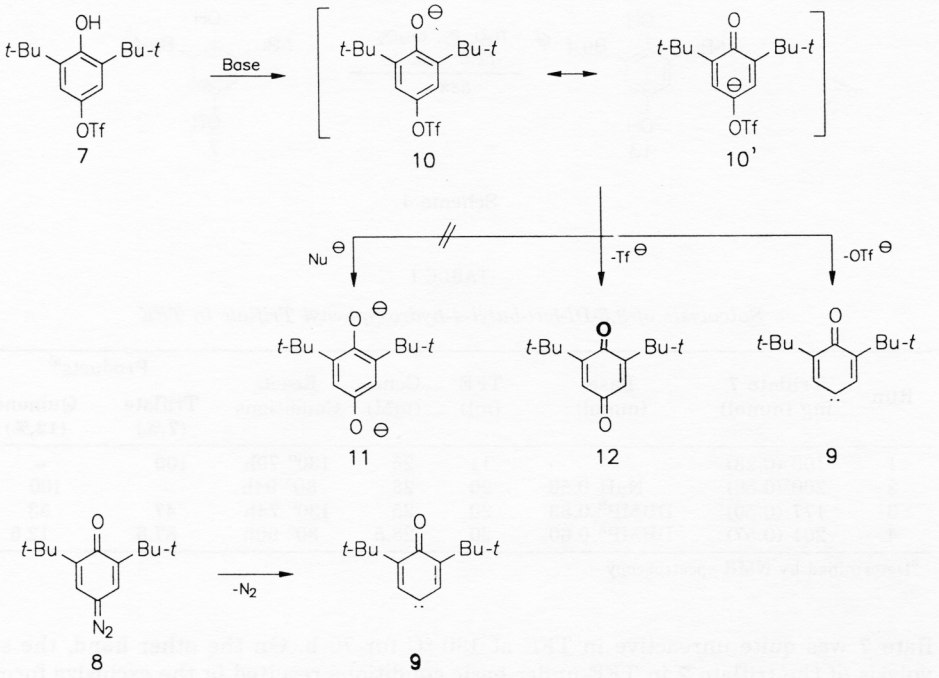
Accordingly we examined the solvolysis of 3,5-di-*tert*-butyl-4-hydroxyphenyl triflate (**7**) (Scheme 3) with an expectation to provide a possible route to the carbene **9** by considering the following points:

(a) formation of the carbene **9** has been well established in thermal and photochemical dediazoniation of the diazooxide **8**,[4]

(b) nucleophilic attack at the sulfur atom of the aryloxy anion **10** generated from **7** might be unfavorable, because such an attack will result in the formation of an unstable dianion **11**, and

(c) the electron density of the *ipso*-carbon atom bearing the triflate group of **10** is increased by *p*-oxide anion as shown in a canonical form (**10'**), which might be expected to promote elimination of the triflate group from **10** to the carbene **9**.

Unexpectedly, however, we report here that the solvolysis of the triflate **7** under basic conditions or the solvolysis of the sodium salt of the oxide ion **10** did not give any products derived from the carbene **9**, but exclusively 2,6-di-*tert*-butylbenzoquinone (**12**) which is considered to have formed as a result of novel elimination of the triflinate group from the triflate **7** (Scheme 3).



Scheme 3

RESULTS AND DISCUSSION

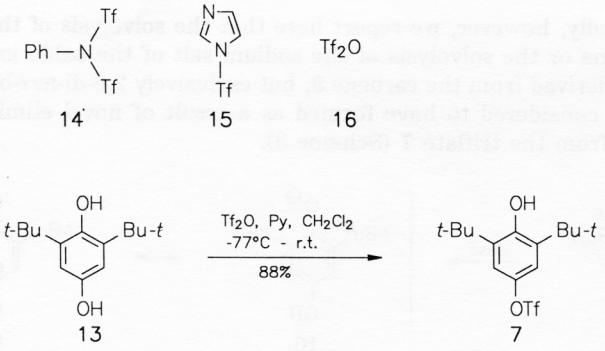
*Preparation of 3,5-di-*tert*-butyl-4-hydroxyphenyl triflate (7)*[5]

The preparation of the triflate **7** from 2,6-di-*tert*-butyl-4-dihydroxybenzene (**13**) was examined by treating with three different triflating reagents; *N,N*-bis(trifluoromethanesulfonyl)aniline (**14**), *N*-trifluoromethanesulfonylimidazol (**15**), and trifluoromethanesulfonic (triflic) anhydride (**16**), in which only the last one was successful (Scheme 4).

A dichloromethane solution of 2,6-di-*tert*-butyl-1,4-dihydroxybenzene (**13**) with a slightly excess amount of pyridine was treated with an equimolar amount of triflic anhydride (**16**) at –77 °C to afford the triflate **7** in 88% yield.

*Solvolysis of 3,5-di-*t*-butyl-4-hydroxyphenyl triflate (7)*

In order to avoid a possible nucleophilic attack of solvents at the sulfur atom of triflate group, trifluoroethanol (TFE), a solvent of high ionizing power and low nucleophilicity was used as a solvent for the solvolysis of triflate **7**. The results of the solvolysis of triflate **7** in TFE are shown in Table I. Under neutral conditions, the tri-



Scheme 4

TABLE I

Solvolysis of 3,5-Di-tert-butyl-4-hydroxyphenyl Triflate in TFE

Run	Triflate **7** mg (mmol)	Base (mmol)	TFE (ml)	Conc. (mM)	React. Conditions	Products[a)] Triflate (**7**,%)	Products[a)] Quinone (**12**,%)
1	100 (0.28)	–	11	25	130° 70h	100	–
2	200 (0.56)	NaH 0.56	20	28	80° 94h	–	100
3	177 (0.50)	DBMP[a] 0.53	20	25	130° 74h	47	53
4	201 (0.57)	DBMP[a] 0.60	20	28.5	80° 90h	87.5	12.5

[a]Determined by NMR spectroscopy.

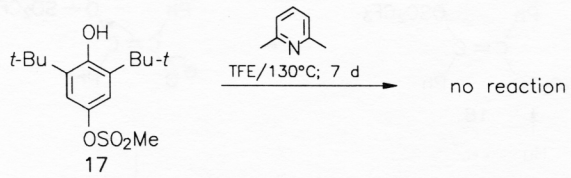
flate **7** was quite unreactive in TFE at 130 °C for 70 h. On the other hand, the solvolysis of the triflate **7** in TFE under basic conditions resulted in the exclusive formation of 2,6-di-*tert*-butylbenzoquinone (**12**).

Solvolyses of **7** in TFE with equimolar amount of 2,6-di-*tert*-butyl-4-methylpyridine (DBMP) at 80 °C for 90 h and at 130 °C for 70 h resulted in 12.5% and 53% conversions of **7**, respectively, both of which gave 2,6-di-*tert*-butylbenzoquinone (**12**) exclusively. Sodium oxide of **7** was prepared by treating **7** with sodium hydride in anhydrous ether and solvolyzed in TFE at 80 °C for 94 h to give the benzoquinone **12**.

2,6-Di-*tert*-butyl-1,4-dihydroxybenzene (**13**) was quite stable even on heating with equimolar amount of pyridine in TFE at 130 °C for 72 h. This result excludes the possibility that the benzoquinone **12** would have subsequently formed by the oxidation of **13** which could be generated by nucleophilic attack of a conjugated base of TFE at the sulfur atom of the triflate group of **7** followed by S–O bond fission.

In contrast to the triflate **7**, the corresponding methanesulfonate (mesylate) was quite stable under similar solvolytic conditions (Sheme 5). 3,5-Di-*tert*-butyl-4-hydroxylphenyl mesylate (**17**) was recovered intact even after heating with a equimolar amount of 2,6-lutidine in TFE at 130 °C for one week.

According to these results, the exclusive formation of the benzoquinone **12** in the solvolysis of the triflate **7** in TFE under basic conditions can be considered as a result of elimination of a triflinate anion from the aryloxy anion **10** of the triflate **7**.



17

Scheme 5

TABLE II

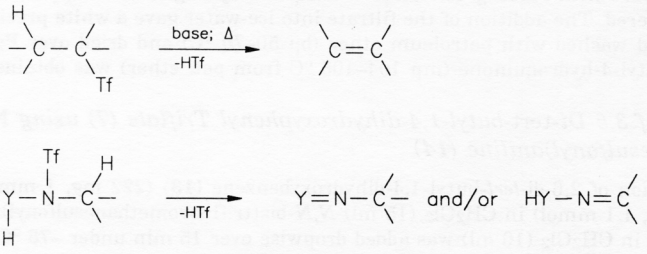
Conmparison of pK_a Values: RSO_2Z

R	Z			
	CH_3[a]	$NH2$[a]	OH	Hc
Ph	29.0	16.7	0.70	2.76
CF_3	18.8	9.75	−11[b] (0.31)[a]	0

[a] DMSO. Permutations of Y–Z–Tf
[b] HOAc. Z=C; Triflones (Y = C, S), Z=N; Triflamides (Y = C, N, O)
[c] H_2O. Z=O; Triflates (Y = C, N, O, P, S).

The triflinate ion is known as an unusually stable sulfinate anion due to the large electronegative effect of the trifluoromethyl group (Table II).

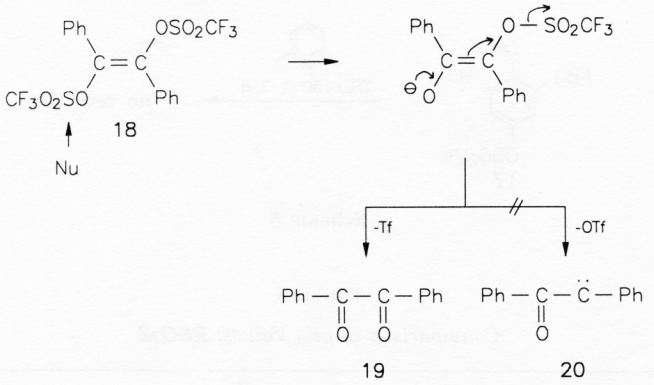
To date, elimination of the triflinate anion is known only in basic β-elimination and thermolysis of triflones and triflamides (Scheme 6).



Scheme 6

On the other hand, the leaving group in the reactions of the triflate compounds has not been the triflinate anion but always the triflate anion,[6] because the triflate anion is much more stable than the triflinate anion (see Table II). The novel elimination of the less stable triflinate anion from the oxide anion **10** to give the stable benzoquinone **12** might be energetically favorable compared with the elimination of the stable triflate anion but to give the very unstable intermediate carbene **9**.

A recent result of the solvolysis of vinyl-1,2-ditriflate **18** by Maas *et al.*[7] can be similarly explained, where nucleophilic attack at the sulfur atom of the first triflate group resulted in subsequent elimination of the triflinate anion form the second tri-



Scheme 7

flate group to give benzoin **19** but not to give the α-ketocarbene **20** by elimination of the triflate anion (Scheme 7).

EXPERIMENTAL

Trifluoromethanesulfonylimidazole,[8] trifluoromethanesulfonic anhydride,[5] and *N,N*-bis(trifluoromethanesulfonyl)aniline[9] were prepared by known methods and purified by distillation and recrystallization, respectively.

*Preparation of 3,5-di-*tert*-butyl-1,4-dihydroxybenzene (13)*

To a solution of 2,6-di-*tert*-butylbenzoquinone (**12**)[10] (5.0 g, 22.7 mmol) in methanol (100 ml) containing zinc powder (5.0 g) was added dropwise conc. hydrochloric acid (25, ml) under ice-water temperature with stirring. After the evolution of hydrogen had stopped, the excess of zinc powder was filtered. The addition of the filtrate into ice-water gave a white precipitate. The solid was filtered and washed with petroleum ether (bp 50–70 °C) and dried over P_2O_5. 4.5 g (89%) of 2,6-di-*tert*-butyl-4-hydroquinone (mp 104–105 °C from pet. ether) was obtained.

*Preparation of 3,5-Di-*tert*-butyl-1,4-dihydroxyphenyl Triflate (7) using* N,N-*Bis(trifluoromethanesulfonyl)aniline (14)*

To a solution of 2,6-di-*tert*-butyl-1,4-dihydroxybenzene (**13**) (222 mg, 1 mmol) and triethylamine (111 mg, 1.1 mmol) in CH_2Cl_2 (15 ml) *N,N*-bis(trifluoromethanesulfonyl)aniline (**14**) (393 mg, 1.1. mmol) in CH_2Cl_2 (10 ml) was added dropwise over 15 min under –78 °C. After the solution was stirred for 2.5 h at –78 °C, the mixture was brought to room temperature and water (30 ml) was added. The CH_2Cl_2 layer was washed with water and dried over sodium sulfate. Evaporation of the solvent gave a solid. Column chromatography of this pasty solid over neutral silica gel (hexane-benzene, 1:1) gave 2 fractions. Fraction 1. 204 mg [mp 97–100 °C recovered *N,N*-bis(trifluoromethanesulfonyl)aniline], and fraction 2.96 mg (mp 67–68 °C, **13**). The required triflate was not obtained.

The preparation of the triflate was similarly attempted by stirring a solution of **13** (222 mg, 1.1 mol) and **14** in anhydrous pyridine (3 ml) at room temperature for 38 h. The work-up of the reaction mixture gave, however, a small amount of recovered hydroquinone (51 mg) and a complex mixture.

The preparation of 4-hydroxyphenyl triflate with **13** (1.1 g, 10 mmol), triethylamine (0.3 ml, catalyst), and *N*-trifluoromethanesulfonylimidazole (**15**) (2.0 g, 10 mmol) in anhydrous ether (20 ml) under room temperature by stirring the mixture for one day was also examined, but hydroquinone was recovered unchanged.

Further work with *N,N*-bis(trifluoromethanesulfonyl)aniline or *N*-trifluoromethanesulfonylimidazole was therefore abandoned.

*Preparation of 3,5-Di-*tert*-butyl-4-hydroxylphenyl Triflate (**7**) with Trifluoromethanesulfonic Anhydride (**16**)*

To a solution of **13** (2.92 g, 13.1 mmol) and pyridine (1.15 g, 14.5 mmol) in CH_2Cl_2 (23 ml) was added dropwise freshly prepared triflic anhydride (**16**) (4.09 g, 14.5 mmol) in CH_2Cl_2 (18 ml) over 20 min at –77 °C. The red-yellow solution was stirred for 24 h at room temperature. After 2 *N*-hydrochloric acid solution (25 ml) was added the solution was extracted with ether and washed with water. Red colour of the ether layer was removed through a column of sodium sulfate and a small amount of neutral silica gel layer. Evaporation of ether gave a solid which was washed with petroleum ether. From the mother liquid which was purified through column over a small amount of silica gel, a solid was obtained. Total yield 4.07 g (87.7%) of 3,5-di-*tert*-butyl-4-hydroxylphenyl triflate [mp 86.2–87.0 °C, recrystallized from petroleum ether, (bp 50–70 °C)]. MS: *m/z* (%); 354 (14); 339 (M^+ –CH_3, 13); 311 (8); 221 (M^+ –SO_2CF_3, 100); 178 (6); 163 (13); 149 (18); 135 (6); 121 (5); 91 (9); 57 (28). ^1H NMR ($CDCl_3$): δ = 1.38 (s, 18H, CH_3), 5.30 (s, 1H, exchangeable with D_2O), 7.01 (s, 2H, ring protons), IR (KBr): ν = 3700 (OH), 1425, 1250, 1220, 1135 cm^{-1} (SO_2CF_3).

Anal. Calc. for $C_{15}H_{21}F_3O_3S$ (M_r = 354.40): C 50.84, H 5.97, S 9.05%; found: C 51.57, H 6.58, S 10.18%.

This triflate decomposes slowly when allowed to stand at room temperature.

*Solvolysis of 3,5-Di-*tert*-butyl-4-hydroxylphenyl Triflate (**7**) in TFE*

Without Base: A solution of the triflate (100 mg, 0.28 mmol, 25 mmol) in TFE (11 ml) was heated at 130 °C for 70 h. The NMR spectrum of the reaction mixture showed that the triflate was recovered unchanged.

*With 2,6-Di-*tert*-butyl-4-methylpyridine:* A solution of the triflate (177 mg, 0.5 mmol, 25 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (109 mg, 0.53 mmol) in TFE (20 ml) was heated in a sealed tube at 130 °C for 70 h. The NMR spectrum of the reaction mixture showed the remained triflate (47%) and 2,6-di-*tert*-butylbenzoquinone (**12**) (52%).

In a similar way a solution of the triflate **7** (201 mg, 0.57 mmol, 28.5 mM) with DBMP (124 mg, 0.60 mmol) was refluxed at 80 °C for 90 h. 12.5% of **12** was obtained and 87.5% of the triflate **7** was recovered.

With Sodium Hydride: Sodium hydride (80% in oil, 16.8 mg, 0.56 mmol) was washed twice with anhydrous ether (2 × 5 ml) and suspended in anhydrous ether (5 ml). The triflate **7** (200 mg, 0.56 mmol) in anhydrous ether (5 ml) was added dropwise to this suspension with stirring (*in situ*-formed sodium phenoxide was insoluble in ether). After the evolution of hydrogen had stopped anhydrous benzene (5 ml) was added. The solution became homogeneous. By decantation the benzene solution was transferred to another flask in order to remove the residual solid and benzene was evaporated in vacuo (20 mmHg). The addition of TFE (17 ml) to a dark-blue residual solid gave a yellow solution with a little amount of white solid (traces of liquid paraffin from commercial sodium hydride). After an additional amount of TFE (3 ml) was added, the yellow solution was refluxed at 80 °C for 94 h under nitrogen atmosphere. The NMR spectrum of the reaction mixture showed the quantitative formation of **12**.

*Solvolysis of 2,6-Di-tert-butyl-1,4-hydroxybenzene (**13**) with Pyridine in TFE*

A solution of 2,6-di-*tert*-butyl-1,4-hydroxybenzene (**13**) (111 mg, 0.5 mmol, 33 mmol) and pyridine (40 mg, 0.5 mmol) in THF (15 ml) was heated in a sealed tube (under nitrogen atmosphere) at 130 °C for 72 h. The NMR spectrum of the reaction mixture showed that 2,6-di-*tert*-butylbenzoquinone (**12**) was not formed, and the hydroquinone **13** was recovered unchanged.

*Preparation of 3,5-Di-*tert*-butyl-4-hydroxyphenyl Methanesulfonate (**17**)*

To an ice-cooled solution of 2,6-di-*tert*-methyl-1,4-dihydroxybenzene (**13**) (1.11 g, 5 mmol) in anhydrous pyridine (2 ml) was added dropwise methanesulfonyl chloride (0.58 g, 5.1 mmol) in anhydrous pyridine (3 ml), and the solution was stirred overnight at room temperature. After water was added to the reaction mixture, the precipitated solid was filtered, washed with water, a little of dilute hydrochloric acid and water, and dried over phosphorous pentoxide. Recrystallization of the solid from petroleum ether (bp 50–70 °C) gave 3,5-di-*tert*-butyl-4-hydroxyphenyl methanesulfonate (**17**) (1.47 g, 98%, mp 139–140 °C, Ref. 10. mp 134–140 °C).

*Solvolysis of 3,5-Di-*tert*-butyl-4-hydroxyphenyl Methanesulfonate (**17**) with 2,6-Lutidine in TFE*

A solution of the methanesulfonate **17** (150 mg, 0.5 mmol) with 2,6-lutidine (53.5 mg, 0.5 mmol) in TFE (20 ml) was heated in a sealed tube at 130 °C for 1 week. The NMR spectrum of the reaction mixture showed that the methanesulfonate was completely recovered unchanged.

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SAŽETAK

Novi mehanizam cijepanja veze S–O u solvolizi aril-triflata

Takaaki Sonoda, Antonio Garcia Martinez, Michael Hanack i L. R. Subramanian

Nađeno je da solvoliza 3,3-di-*tert*-butil-4-hidroksifenil-triflata (**7**) u trifluoretanolu u prisutnosti nenukleofilne baze 2,6-di-*tert*-4-metilpiridina kao pufera teče izuzetno brzo. Opaženi fenomen pripisan je novom tipu eliminacije triflat-aniona iz konjugirane baze triflata **7** pri čemu nastaje 2,6-di-*tert*-butil-1,4-benzokinon.