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SOLVOLYSIS OF SPIRO[2.5]OCTA-1,4,7-TRIEN-6-ONES EVIDENCE OF A VINYL CATION INTERMEDIATE

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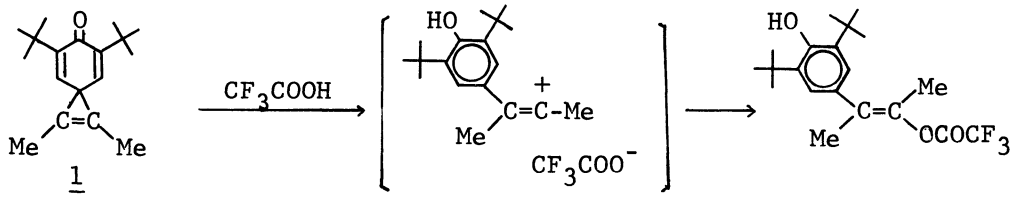
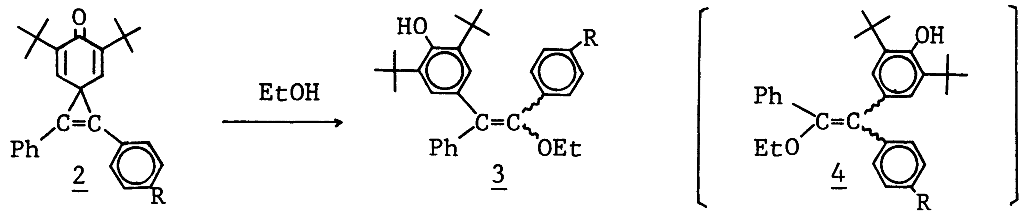
Ethanolysis of 1-aryl-5,7-di-t-butyl-2-phenylspiro[2.5]octa-1,4,7-trien-6-one 2 proceeds via a vinyl cation generated by opening of the cyclopropene ring, judging from regiospecific ring opening and kinetics (ρ^{+}= -3.0, m= 0.53, and rate dependence on pH of the solvent).

A vinyl cation has widely been recognized as one of reactive intermediates.$^{1)}$ The usual methods to generate a vinyl cation are i) heterolysis of vinyl derivatives and ii) electrophilic addition to acetylenic or allenic compounds. Pirkle et al. suggested intervention of a vinyl cation in the reaction of 1,2-dimethylspiro[2.5]octatrienone 1 with trifluoroacetic acid.$^{2)}$ To clarify generation of a vinyl cation in such a reaction we examined the reaction of 1-aryl-5,7-di-t-butyl-2-phenylspiro[2.5]octa-1,4,7-trien-6-one 2 $^{3)}$ under solvolytic conditions. Spiro[2.5]octatrienone 2 must be much more adequate system to study than 1, since 2 gives α-arylvinyl cation which is much more stable than α-methylvinyl cation from 1. Changing the aryl group may give a criterion for formation of a vinyl cation.



We will show here evidence for generation of a vinyl cation in solvolysis of spiro[2,5]octatrienone 2.

The reaction of spiro[2.5]octatrienone 2a (113 mg, 0.27 mmol) in ethanol (10 ml) at a room temperature for 38 h gave a 1:1 mixture of E- and Z-vinyl ethyl ether 3a quantitatively.[4)] Vinyl ethyl ether 4a, the isomer of 3a, could not be detected in the reaction mixture at all. Similar treatment of 2b and 2c also gave only vinyl ethyl ether 3b [E/Z(or Z/E)= 45/55] and 3c≡4c [E/Z(or Z/E)= 43/57], respectively. The formation of 3a,b without 4a,b shows a regiospecific opening of the cyclopropene ring.



a : R = OMe, b ; R = Me, c : R = H

The reaction rates of the solvolysis of 2 were measured and the first-order rate constants are shown in Table 1 and 2. The reaction of 2a was accelerated with increasing the content of water in the solvent. The solvent effect relatively well correlated with the Grunwald-Winstein's Y-value (m= 0.53 in aqueous ethanol at 30 °C). A large substituent effect was observed; k_{rel}= 1.0: 4.2: 380 for 2c: 2b: 2a (ρ^+= -3.0). In basic conditions the rate constants were unchanged but in more acidic conditions (pH <10.5) the rate increased as the pH decreased.

The above results substantiate the formation of vinyl cation 6 as the reactive intermediate in the solvolysis of spiro[2.5]octatrienone 2. Vinyl cation 6 should come from opening of the cyclopropene ring, both C-C bonds of which are weakened by protonation or hydrogen bonding on the carbonyl oxygen as shown in 5. The solvent effect is agreement with those in solvolysis of vinyl derivatives (*e.g.* m= 0.53 for $An_2C=C(Cl)An$ in 80-65% aq.EtOH)[5)] and the substituent effect is a little bit small[6)] but comparable with those in solvolysis of vinyl derivatives (ρ^+= -4.1 for $CH_2=C(OSO_2CF_3)Ar$)[7)] and in acid-hydrolysis of acetylenic compounds (ρ^+= -3.8 for $ArC{\equiv}CH/H_2SO_4$).[8)] The pH of the solvent must largely influence the reaction rates, because vinyl cation 6 results from protonation of 2. The regiospecific ring opening is consistent with the stability of the resultant vinyl cation, that is, the formation of vinyl cation 6 rather than 7. A triarylvinyl cation like 6 usually has a linear structure to which nucleophile(s) can attack from the both directions, so that a 1:1 mixture of E- and Z- vinyl derivatives is formed.[9)] Therefore, the formation of a ca. 1:1 mixture of E- and Z-vinyl ethyl ether 3 also supports the formation of vinyl cation 6 as the reactive intermediate in the solvolysis of 2.

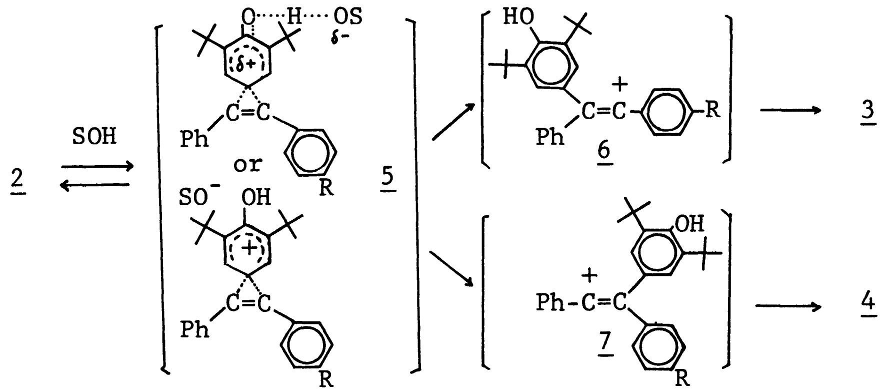


Table 1. Kinetics of the solvolysis of 2 in aqueous ethanol.

Compound	Solvent/% EtOH	Temp/°C	k/10^4 s^{-1} a)
2a	100	30	0.792 ± 0.054
	90	20	0.731 ± 0.003
	90	30	2.58 ± 0.01
	90	40	6.79 ± 0.45
	90	70	123$^{c)}$
	80	30	8.31 ± 0.36
	70	30	18.9 ± 6.6
	b)	30	2.19 ± 0.01
2b	90	70	1.37 ± 0.03
2c	90	70	0.653 ± 0.012 (0.327)$^{d)}$

a) All reactions were followed spectroscopically at 340 nm for 2a, 330 nm for 2b and 2c. All rate constants are an average of duplicated determinations.
b) Absolute methanol. c) Extrapolated from the data at lower temperature.
d) Corrected statistically.

Table 2. Kinetics of 2a in methanol$^{a)}$ at 25 °C

Added Solutes	Conc/10^3 mol l^{-1}	pH$^{b)}$	k/10^4 s^{-1} c)
CH_3COOH/CH_3COONa	43.7/40.3	9.728	383 ± 19
CH_3COOH/CH_3COONa	31.6/41.6	9.762	359 ± 2
CH_3COOH/CH_3COONa	27.2/48.2	9.820	201 ± 3
CH_3COOH/CH_3COONa	2.50/60.5	10.00	15.6 ± 0.7
CH_3COONa	0.61	13.48	0.558± 0.002
CH_3ONa	12.1	14.78	0.516± 0.002
CH_3ONa	121	15.78	0.543± 0.006

a) As the solvents, 99.34% MeOH-0.66% Et_2O was used. b) According to ref. 10.
c) All reactions were followed spectroscopically at 336 nm. All rate constants are an average of duplicated determinations.

References

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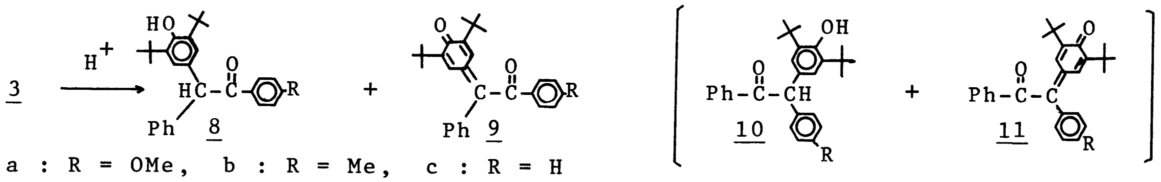
4) NMR spectra* of 3. 3a; δ 1.12(t,J=7 Hz,3H), 1.18 and 1.36(s,18H), 3.60(q,J=7 Hz,2H), 3.68 and 3.69(s,3H), 4.85 and 4.98(s,3H), 6.47-7.46(m,11H). 3b; δ 1.20(t, J=7 Hz,3H), 1.12 and 1.35(s,18H), 2.22(s,3H), 3.44(q,J=7 Hz,2H), 4.77 and 4.91(s,1H), 6.44-7.40(m,11H). 6c; δ 1.22(t,J=7 Hz,3H), 1.12 and 1.34(s,18H), 3.56(q,J=7 Hz, 2H), 4.77 and 4.90(s,1H), 6.49-7.80(m,12H). The structure of these vinyl ethyl ether 3 was further confirmed by acid-hydrolysis, which gave ketone 8 and its oxidized product 9. There was no ketones 10 and 11 expected from vinyl ethyl ether 4 even in the mother liquor after isolation of 8 and 9. The structure of 8 and 9



a : R = OMe, b : R = Me, c : R = H

which has a p-substituted benzoyl group were distinguished from those of 10 and 11 which has a benzoyl group by NMR(arom.) and MS($ArCO^+$) spectra. Spectra data* and mp of 8 and 9. 8a; 158-160°C. δ 1.38(s,18H), 3.80(s,3H), 5.00(s,1H), 5.79(s,1H), 6.84-8.06(m,11H). ν_{max} 3521, 1670 cm^{-1}. λ_{max} 272 nm(log ε, 4.31), 230(4.90,sh). 8b; 164-166°C. δ 1.35(s,18H), 2.31(s,3H), 4.85(s,1H), 5.67(s,1H), 6.84-7.85(m,11H). ν_{max} 3612, 1679 cm^{-1}. λmax 275 nm(log ε, 3.66), 254(4.24), 241(4.21). 8c; 119-123°C. δ 1.35(s,18H), 4.87(s,1H), 5.70(s,1H), 6.80-7.95(m,12H). ν_{max} 3560, 1672 cm^{-1}. λ_{max} 282 nm(log ε, 3.43,sh), 272(3.45), 237(4.27). 9a; 171-173°C. δ 1.12 (s,9H), 1.20(s,9H), 3.80(s,3H), 6.75-8.00(m,11H). ν_{max}1646,1618, 1610 cm^{-1}. λ_{max} 338 nm(log ε, 3.42), 310(4.29),274(4.23). 9b; 169-170°C. δ 1.08(s,9H), 1.20(s, 9H), 3.80(s,3H), 6.75-8.00(m,11H). ν_{max} 1657, 1623, 1615, 1605 cm^{-1}. λ_{max} 338 nm (log ε, 4.41), 251(4.22). 9c; 142-145°C. δ 1.08(s,9H), 1.20(s,9H),6.60-8.00(m,12 H). ν_{max} 1665, 1643, 1619, 1609 cm^{-1}. λ_{max} 338 nm(log ε, 4.39), 244(4.20). The structure of 8 and 9 was also established by elementary analysis and MS spectra.

* NMR spectra were measured in CCl_4 with TMS as an internal standard, IR with nujol, and UV in cyclohexane.

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6) Cationic character of the developing vinyl cation must be dispersed by perturbation like a phenonium ion, which must lead to a relatively small ρ^+ value.

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