CHEMISTRY LETTERS, pp. 391-394, 1982. © The Chemical Society of Japan 1982

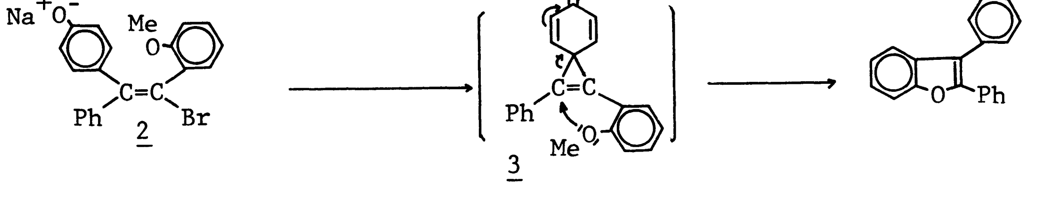
A NEIGHBOURING GROUP PARTICIPATION OF *ORTHO*-METHOXYL GROUP IN SOLVOLYTIC REACTION OF SPIRO[2.5]OCTA-1,4,7-TRIEN-6-ONES

Toshihiko IKEDA, Shinjiro KOBAYASHI, and Hiroshi TANIGUCHI*
Department of Applied Chemistry, Faculty of Engineering,
Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812

In aqueous ethanol 1-aryl-5,7-di-t-butyl-2-(o-methoxyphenyl)-spiro[2.5]octa-1,4,7-trien-6-one 4 changed to 2-aryl-3-(3',5'-di-t-butyl-4'-hydroxyphenyl)benzofuran 5 in a more than 90% yield. The selective formation of 5 is ascribed to a neighbouring group participation of the *ortho*-methoxyl group to an incipient vinyl cation.

There are many examples of neighbouring group participations which are one of the most interesting subjects in the chemistry of trivalent carbocations.[1)] However, there are only a few examples[2,3)] in the chemistry of vinyl cations which have been well-established.[4)] We reported exclusive formation of benzofuran derivatives without an anchimeric acceleration by the *ortho*-methoxyl group in the solvolysis of vinyl bromide 1,[5)] while we suggested a neighbouring group participation of the methoxyl group in the reaction of spiro[2.5]octatrienone 3 which was intervenient in the solvolysis of vinyl bromide 2.[6)]

We would like to report here evidence for a neighbouring group participation



of the *ortho*-methoxyl group in the solvolytic reaction of 1-aryl-5,7-di-t-butyl-2-(o-methoxyphenyl)spiro[2.5]octa-1,4,7-trien-6-one 4.7)

The reaction of spiro[2.5]octatrienone 4c (0.17 mmol) in ethanol (10 ml) at ambient temperature for 36 h gave benzofuran 5c.8) Similar treatments of 4a, 4b, and 4d also gave 5a, 5b, and 5d, respectively, as shown in Table 1. In all cases benzofuran 5 was obtained in a more than 90% yield, while the solvent-incorporated products, the vinyl ethyl ethers and the ketones, could not be detected. Benzofuran 5 was formed by breaking the specific C-C bond of the cyclopropene ring(path a). However, under acidic conditions the reaction of 4c gave not only 5c but also a product through the other C-C bond cleavage(path b). For instance, the mixture of 4c (0.3 mmol), ethanol (9 ml), and trifluoroacetic acid (1 ml) was kept to stand at a room temperature for 46 h, and after evaporation of the solvent with a water pump 5c and ketone 68) were obtained in 86 and 14% yields, respectively.

To reveal the reaction mechanism for the selective formation of benzofuran 5 the reaction rates of 4 were measured and the obtained first-order rate constants are shown in Table 2 and 3. The reaction was accelerated by substitution of an electron donating group (MeO>Me>H>Br). The Hammett plots against σ^+ afforded a negative ρ^+, -2.3. Furthermore, a rate enhancement was observed with increasing water content in the solution, and a Grunwald-Winstein's m-value, 0.45, was calculated. As shown in Table 3 the rate constants were unchanged in basic solutions but in more acidic solutions (pH <10.5) the rate increased as the pH decreased. The degree of these effects in a substituent, solvent polarity, and solvent's pH were lower than those in the solvolysis of spiro[2.5]octatrienone 7 to generate vinyl cation 8 (ρ^+= -3.0, m= 0.53, and 670 time-faster rate in pH 9.75 than in pH

Table 1 Products of spiro[2.5]octa-1,4,7-trien-6-ones

Compound	Solvent	5 (%)*	6 (%)*	** (%)*
4a	97% EtOH-3% H_2O	100	0	0
4b	100% EtOH	98	0	2
4c	100% EtOH	96	0	4
	EtOH (9 ml) + 0.1N-NaOH (1 ml)	96	0	4
	EtOH (9 ml) + TFA (1 ml)***	86	14	0
	EtOH (4 ml) + TFA (1 ml)	74	26	0
4d	100% EtOH	90	0	10

* Product distribution was determined by NMR analysis.

** Unidentified product(s). *** Trifluoroacetic acid.

15, respectively).[9)] These phenomena are well explained by considering an anchimeric assistance of the *ortho*-methoxyl group in the formation of benzofuran 5. Hydrogen bonding or protonation on the carbonyl oxygen perturbs the cyclopropene ring to weaken both C-C bonds of the ring. Judging from the results in the solvolysis of 7, bond b must break more easily than bond a to give more stable vinyl cation in cases of 4b-d. However, the cleavage of bond a occures faster than that of bond b. The cleavage of bond a should be caused by an intramolecular nucleophilic attack of the *ortho*-methoxyl group, that is, a neighbouring group participation. This mechanism is also consistent with the following results; i) the relative rate of 4c to 7c, both of which are considered to generate α-phenylvinyl cations, was 336 and ii) the extent of cleavage of bond a to bond b was larger in a basic solution than in an acidic solution, because the neighbouring group particicipation should depend on the perturbation of the bond a, that is, the neighbouring group participation must be more effective in case of hydrogen bonding (in a basic solution) than in case of protonation.

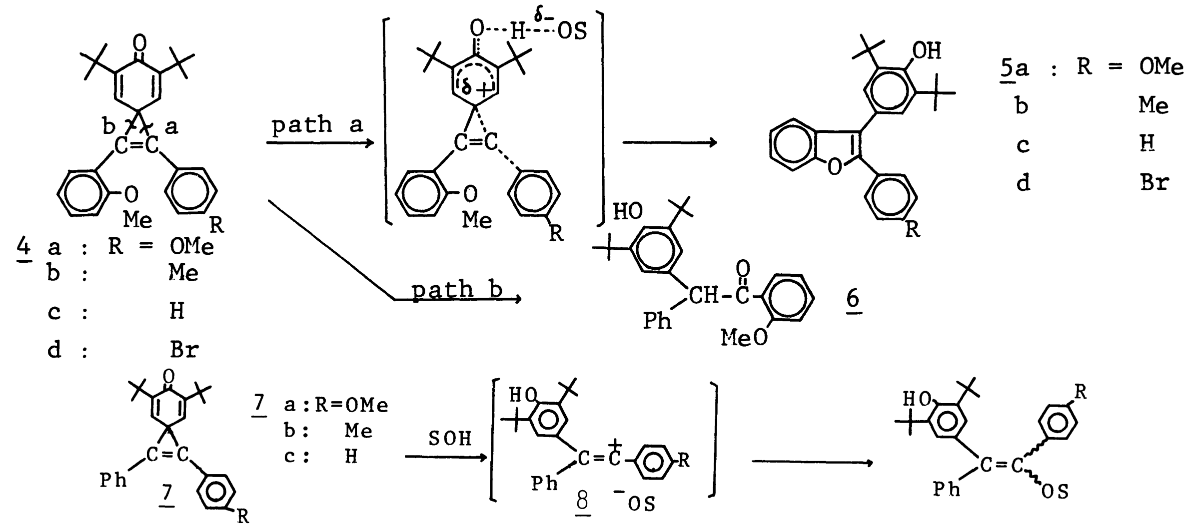


Table 2 Kinetics of 1-aryl-5,7-di-t-butyl-2-phenyl- and 5,7-di-t-butyl-1,2-diphenylspiro[2.5]octa-1,4,7-trien-6-ones in aqeous ethanol

Compound	Solvent/% EtOH	Temp/ °C	$k/10^4$ s^{-1} a)
7a	90	20	87.0 ± 2.3$^{b)}$
7b	90	20	12.1 ± 0.2
	90	20	12.4 ± 0.5$^{b)}$
7c	70	20	10.6 ± 0.4
	80	20	6.36 ± 0.53
	90	20	1.92 ± 0.05
	100	20	0.781 ± 0.028

(Continued)

	90	25	3.00 ± 0.05
	90	30	4.89 ± 0.21
	90	70	110[c)]
<u>4d</u>	90	20	0.637 ± 0.029
<u>7c</u>	90	70	0.635 ± 0.12[d)] 0.327[e)]

a) All reactions were followed spectrospcopically. b) 0.17% of absolute ether was contained. c) Extrapolated from data at lower temperature. d) Taken from ref. 9). e) Corrected statistically.

Table 3 Kinetics of 1-(p-bromophenyl)-5,7-di-t-butyl-2-(o-methoxyphenyl)-spiro[2.5]octa-1,4,7-trien-6-one <u>4d</u> in absolute methanol at 25 °C

Added Solutes	Conc/ 10^3 mol l^{-1}	pH[a)]	k/10^4 s^{-1} [b)]
CH_3COOH/CH_3COONa	65.0/63.3	9.751	42.5 ± 0.3
CH_3COOH/CH_3COONa	47.2/76.0	9.969	31.6 ± 0.3
CH_3COOH/CH_3COONa	29.4/88.7	10.24	17.9 ± 0.1
CH_3ONa	1.90	13.98	2.18 ± 0.04
CH_3ONa	38.0	15.28	2.18 ± 0.01
CH_3ONa	380	16.28	2.33 ± 0.01

a) According to ref. 10). b) All reactions were followed spectroscopically.

References

1) G.A.Olah and P.v.R.Scleyer, Ed.,"Carbonium Ions", Wiley-Interscience, New York, N.Y. Vol. 1-4(1968-1973).

2) A.Burighel, G.Modena, and U.Tonellato, J.Chem.Soc. Perkin II, <u>1972</u>,2026.

3) P.J.Stang and T.E.Deuber, J.Am.Chem.Soc., <u>99</u>,2602(1977).

4) P.J.Stang, Z.Rappoport, M.Hanack, and L.R.Subramanian,"Vinyl Cations", Academic Press, New York, 1979.

5) T.Sonoda, S.Kobayashi, and H.Taniguchi, Bull.Chem.Soc.Jpn, <u>49</u>,2560(1976).

6) H.Ohba, T.Ikeda, S.Kobayashi, and H.Taniguchi, Chem.Comm., <u>1980</u>,988.

7) T.Ikeda, S.Kobayashi, and H.Taniguchi, Synthesis in press.

8) Mp and spectral data. <u>5a</u>; 138-141°C. δ 1.40(s.18H), 5.12(s,1H),7.03-7.80(m,11 H). λ_{max} 304 nm(log ε, 4.25),242(4.32). MS(M^+); 398. <u>5b</u>; 175-177°C. δ 1.41(s,18H), 3.74(s,3H), 5.09(s,1H), 6.54-7.67(m,10H). λ_{max} 313 nm(log ε, 4.37), 248(4.33). MS (M^+) 428. <u>5c</u>; 195-197°C. δ 1.40(s,18H), 2.32(s,3H), 5.07(s,1H), 6.85-7.60(m,10H). λ_{max} 310 nm(log ε, 4.32), 243(4.32). MS(M^+) 412. <u>5d</u>; 221-223°C. δ 1.43(s,18H), 5.15(s,1H),7.05-7.63(m,10H). λ_{max} 326 nm(log ε, 4.35sh), 319(4.35),243(4.32). MS (M^+) 478, 476. <u>6</u>; δ 1.34(s,18H), 3.72(s,3H), 4.98(s,1H), 5.75(s,1H), 6.62-7.87(m, 11H). ν_{max} 3560 and 1670 cm^{-1}. MS(M^+) 430. NMR spectra were measured in CCl_4 with TMS as an internal standard and UV in cyclohexane.

9) T.Ikeda, S.Kobayashi, and H.Taniguchi, under submitting to Chem.Lett.

10) S.Winstein and R.Baird, J.Am.Chem.Soc., <u>85</u>,567(1963).

(Received December 18, 1981)