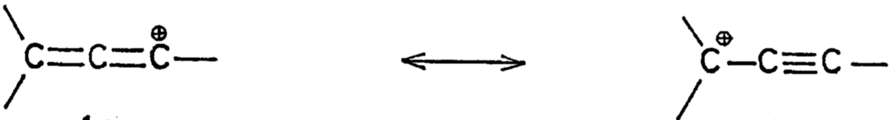
CHEMISTRY LETTERS, pp. 163-166, 1977. Published by the Chemical Society of Japan

SOLVOLYSIS OF BUTATRIENYL HALIDES: EVIDENCE OF AN AMBIDENT VINYL CATION

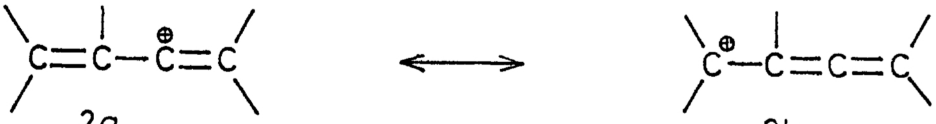
Shinjiro KOBAYASHI, Takaaki SONODA, and Hiroshi TANIGUCHI
Department of Applied Chemistry, Faculty of Engineering,
Kyushu University, Hakozaki, Fukuoka 812

The reactions of butatrienyl halides 4 and 5 in aqueous ethanol exclusively gave bis(benzofuranyl)acetylene 6. The first-order kinetics, the leaving group effect, $k_{Br}/k_{Cl}=52$, and the Grunwald-Winstein's m value of ca. 0.5 show that 4 and 5 are solvolyzed by an S_N1 mechanism. The intermediate carbenium ion 7 is a new type of ambident vinyl cations.

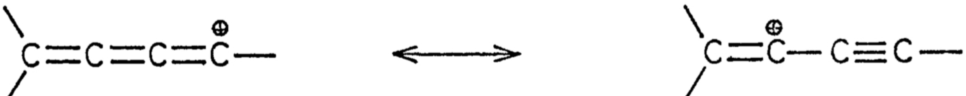
Recent extensive studies of solvolysis of vinyl derivatives made it clear the existence of vinyl cations.$^{1)}$ It was reported that haloallenes$^{2)}$ and 2-bromo-1,3-butadienes$^{3)}$ are solvolyzed under milder conditions than vinyl halides because of the resonance stabilization of the carbenium ion intermediates 1 and 2. The occurrence of the rearranged products derived from 1b and 2b also supports that these carbenium ions are ambident. Notice that one of the mesomeric structures of these ambident carbenium ions is a disubstituted ion (1a and 2a) but the other is a normal trisubstituted ion (1b and 2b). However, the solvolysis of butatrienyl halides might give the ambident vinyl cation 3 which has positive charge on a disubstituted carbon in both mesomeric structures (3a and 3b). The vinyl cation 3b was suggested in view of a stabilized vinyl cation by a triple bond, but has not yet been generated.$^{1a)}$



1a 1b



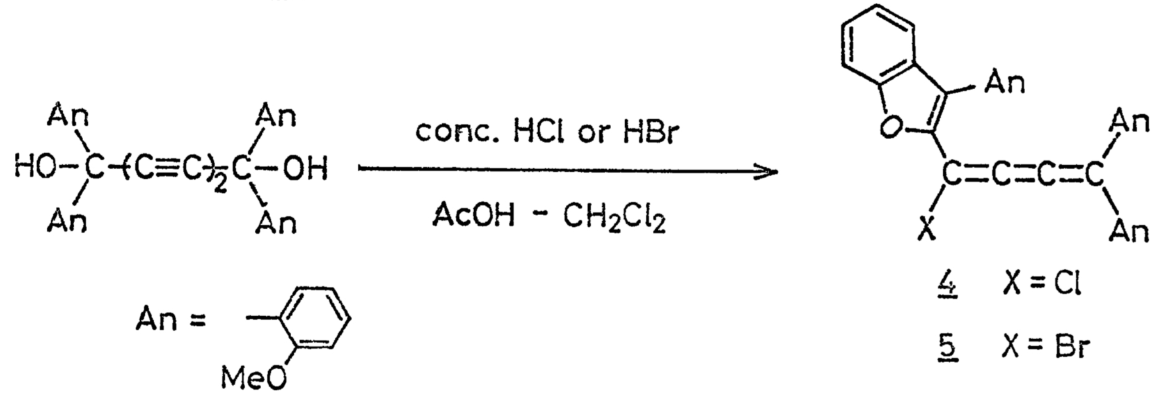
2a 2b



3a 3b

For the preparation of 4,4-bis(o-methoxyphenyl)-1-[3'-(o-methoxyphenyl)-2'-

benzofuranyl]butatrienyl halides 4 and 5, 1,1,6,6-tetrakis(o-methoxyphenyl)-2,4-hexadiyne-1,6-diol was treated with hydrochloric and hydrobromic acid, respectively, in a mixed solvent of acetic acid and methylene chloride[4]. The structures were assigned by the following data: 4: mp 154-155°C; nmr($CDCl_3$) δ 3.65, 3.71, 3.84 (all s, OCH_3), 6.7-7.6 (m, arom. H); uv λ_{max} 440nm(log ε 4.54), 272 (4.44): 5: mp 157-159°C; nmr($CDCl_3$) δ 3.59, 3.69, 3.85 (all s, OCH_3), 6.6-7.4 (m, arom. H); uv λ_{max} 440nm(log ε 4.53), 267 (4.34).[5]

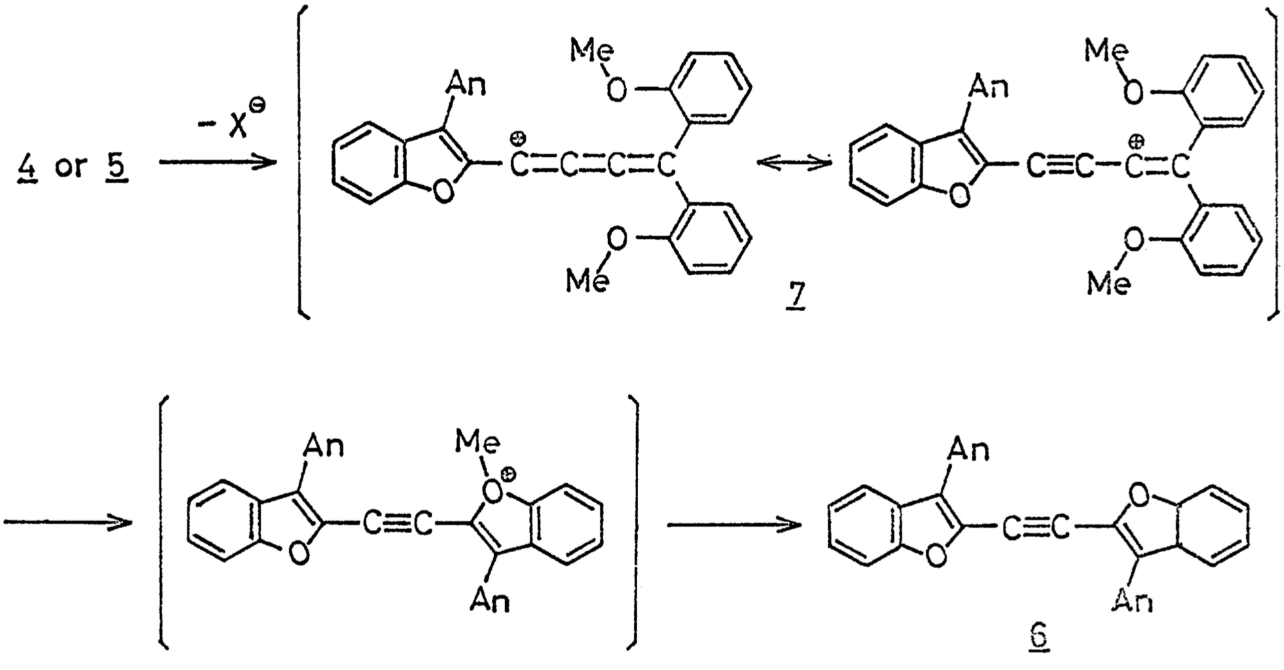


4 X = Cl

5 X = Br

The solvolysis of both 4 and 5 in 80% aqueous ethanol at 60°C afforded the same colorless crystalline compound 6, mp 149-150°C in > 97% yield[6] from 4 and ∿100% yield from 5. The structure of 6 was assigned to bis[3'-(o-methoxyphenyl)-2'-benzofuranyl]acetylene by the following data: nmr(CCl_4) δ 3.70(s, OCH_3), 6.8-7.6 (m, arom. H); uv λ_{max} 360nm(log ε 4.45), 308 (4.32), 238 (4.48). The comparison of the electronic spectrum of 6 with those of bis(benzofuranyl)acetylenes[4] confirmed its structure.

The formation of 6 can be explained by the sequence shown in the following scheme. The ambident vinyl cation 7 generated by the solvolysis is



7

6

intramolecularly attacked by the methoxy group which is located in the suitable position to form the five-membered ring, followed by elimination of the methyl moiety.

The existence of ambident vinyl cation 7 was supported by the following kinetic experiments. The rates of the solvolysis were measured spectrometrically and the results are shown in Table. Excellent first-order kinetics were observed up to 90% reaction and were not affected with or without base. A comparison of the solvolysis rates of 4 and 5 yields a leaving group effect k_{Br}/k_{Cl}=52. This value is similar to those reported for the solvolysis of tris(p-methoxyphenyl)-vinyl bromide and chloride, k_{Br}/k_{Cl}=58[7] and 1,3-di-tert-butyl-3-phenylallenyl bromide and chloride, k_{Br}/k_{Cl}=56[2]. An increase in solvent polarity results in an increase in the rates of solvolysis. A plot of log k for butatrienyl bromide 5 vs. Grunwald-Winstein's Y value is slightly convex and the slope is ca. 0.5 for 60-90% ethanol. This value is similar to those found in the solvolysis of tris(p-methoxyphenyl)vinyl bromide, m=0.34[7] and 3-methyl-2-butenyl triflate, m=0.60[8].

The above results support that butatrienyl halides 4 and 5 are solvolyzed by the S_N1 mechanism via the new type of " ambident vinyl cation " intermediate. It is not easy to mention the stabilization of vinyl cation by a triple bond in this case, because there is no precise estimation of the α-substituent effect of 3-(o-methoxyphenyl)-2-benzofuranyl group.

Further investigation of the solvolysis of butatrienyl halides, which can be compared to those of vinyl halides, is now in progress.

Table. Solvolysis of Butatrienyl Halides 4 and 5 in Aqueous Ethanol [a)]

Compound	Solvent	Temp, °C	k, s^{-1}	
4	80%EtOH	70.0	6.71 $\times 10^{-5}$	
		60.0	(2.77 ± 0.01)	no NaOH
5[b)]	80%EtOH	60.0	(1.43 ± 0.01) $\times 10^{-3}$	no NaOH
			(1.44 ± 0.01)	
			(1.41 ± 0.02)	0.1M LiBr
	90%EtOH	50.0	1.04 $\times 10^{-4}$	
	80%EtOH		(5.17 ± 0.02)	
	70%EtOH		(1.02 ± 0.01) $\times 10^{-3}$	
	60%EtOH		(1.67 ± 0.02)	
	80%EtOH	40.0	(1.57 ± 0.01) $\times 10^{-4}$	0.1M LiBr

a)k is an average of two or more runs in each at an initial concentration of ca. 3×10^{-5} M the halide in the presence of 10^{-4} M NaOH.

b)The activation parameters for the solvolysis of the bromide in 80% ethanol at 50°C; $\Delta H^{\dagger}$ = 22.0 kcal/mole, $\Delta S^{\dagger}$ = -5.6 e.u.

REFERENCES and NOTES

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(Received December 13, 1976)