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Crystallographic Approach to the Origin of "Syn-Effect"[1)]

Katsuhiko INOMATA,* Takaki HIRATA, Yoshihiro SASADA, Takahiro ASADA,
Hitoshi SENDA,† and Hideki KINOSHITA
Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa 920
†Department of Chemistry, College of Liberal Arts, Kanazawa University, Kanazawa 920

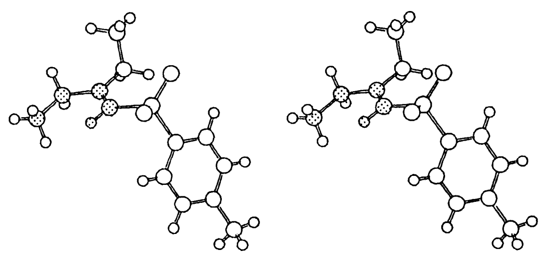
It was revealed by X-ray crystallography that α-unsubstituted (E)-vinyl sulfones have syn-conformation which seems to be the cause of "syn-effect" found in the conversion of (E)-vinyl sulfones to the corresponding allyl sulfones with a base under mild conditions. Syn-conformation of a terminal olefin in solid state was also confirmed.

In the previous papers,[2a,b)] we reported the regio- and stereoselective syntheses of (E)- and (Z)-vinyl sulfones and their conversion to the corresponding allyl sulfones under the mild basic conditions, and it was found that (E)-vinyl sulfone preferentially affords (Z)-allyl sulfone as a kinetically-controlled product, while (Z)-vinyl sulfone and α-substituted vinyl sulfone give (E)-allyl sulfones exclusively. The latter fact may be due to the steric congestion which precludes the possibility of a stabilizing syn-interaction between the α- and δ-positions.[3d)]

The former experimental results were rationalized by the new concept "conformational acidity" (a sort of kinetic acidity),[2a,b)] which essentially depends on a "syn-effect"[3)] within the cases of the conversion discussed so far. The relative degree of the "syn-effect" was further determined by the stereochemical investigation on the conversion of various kinds of γ-substituted (E)-vinyl sulfones with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to the corresponding allyl sulfones as follows: CH_3O- ≥ AcO- > CH_3 > $-CH_2-$ >> t-Bu- and Ph-.[2c)]

Several explanations for the "syn-effect" have been proposed,[3b)] namely (1) 6π-electron homoaromaticity, (2) σ-orbital interactions, (3) dipole-dipole interactions, (4) chelations, and (5) hydrogen bonding.[3e)] Regarding these problems, we have performed X-ray crystallography for 2-ethyl-1-tosyl-1-butene (1), which afforded exclusively (Z)-2-ethyl-1-tosyl-2-butene by treatment with DBU, and found that "syn-effect" worked in 1 itself as shown in Fig. 1.[2c)] Herein we wish to report the new results of the crystallographic studies on the other α-unsubstituted (E)-vinyl sulfones and a crystalline terminal olefin derivative.

Since methoxy group has been proven to be the most effective one for "syn-effect" as described above,[2c)] the conversion of the similar vinyl sulfones, (E)-3-phenoxy- and (E)-3-ethoxy-1-tosyl-1-propenes (2a,b), to the corresponding allyl sulfone derivatives (3a,b) was examined by using DBU as a base. The time-course of the reaction shown in Table 1 revealed that 2a,b afford exclusively (Z)-3a,b, especially at higher selectivity at the initial step of the reaction. These



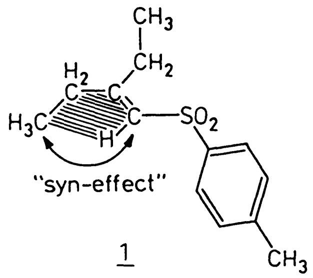


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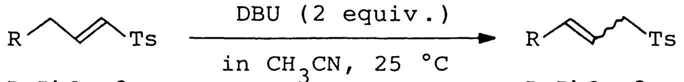
Fig. 1. Stereoscopic view of 2-ethyl-1-tosyl-1-butene (1).

results strongly suggested the possibility that 2a,b have the syn-conformation as well as 1. In order to confirm the structure of 2a, X-ray crystallography was performed (Fig. 2).[4] It was found that H1, C1, C2, C3, O3 and H5, C17, C18, C19, O6 exist on a plane, respectively, and that "syn-effect" works in the solid state of 2a. The syn-conformation seems to arise from the intramolecular hydrogen bonding between the rather acidic α-hydrogens (H1 and H5), neighboring to the electron withdrawing tosyl group, and oxygens (O3 and O6) using the electron pairs of their sp^2 orbitals (O3-H1 2.36 Å, O6-H5 2.39 Å) or dipole-dipole interaction between $C_{sp^2}\leftarrow H$ and $C\rightarrow OR$. However, 6π-electron homoaromaticity should not be excluded in spite of the long distances of O3-C1 (2.72(2) Å) and O6-C17 (2.78(2) Å), because there are p-orbitals on oxygen atoms (O3 and O6) conjugating with a phenyl group, which appear to correspond to the pseudo-p-orbital of the methyl group useful to stabilize syn-conformation of 1 in which the intramolecular hydrogen bonding is impossible.

Though the comparison of the structure of 2b with 2a was therefore required, 2b was oil at

Table 1. Conversion of (E)-3-Phenoxy- and (E)-3-Ethoxy-1-tosyl-1-propenes (2a,b) to the Corresponding 1-Tosyl-2-propene Derivatives (3a,b) with DBU



R=PhO, 2a
R=EtO, 2b

R=PhO, 3a
R=EtO, 3b

2	Time	Products ratio[a]			Isolated total yield of 3/%
		(E)-2	(E)-3	(Z)-3	
2a	0 min	100	0	0	-
	30 min	0	3	97	quant.
	2 h	0	3	97	-
	12 h	0	4	96	-
	96 h	0	8	92	-
2b	0 min	100	0	0	-
	30 min	27	2	71	-
	1 h	6	4	90	-
	2 h	0	5	95	-
	3 h	0	5	95	97
	6 h	0	4	96	-
	24 h	0	4	96	-
	72 h	0	4	96	-

a) Determined by 400 MHz ^{1}H-NMR spectra.

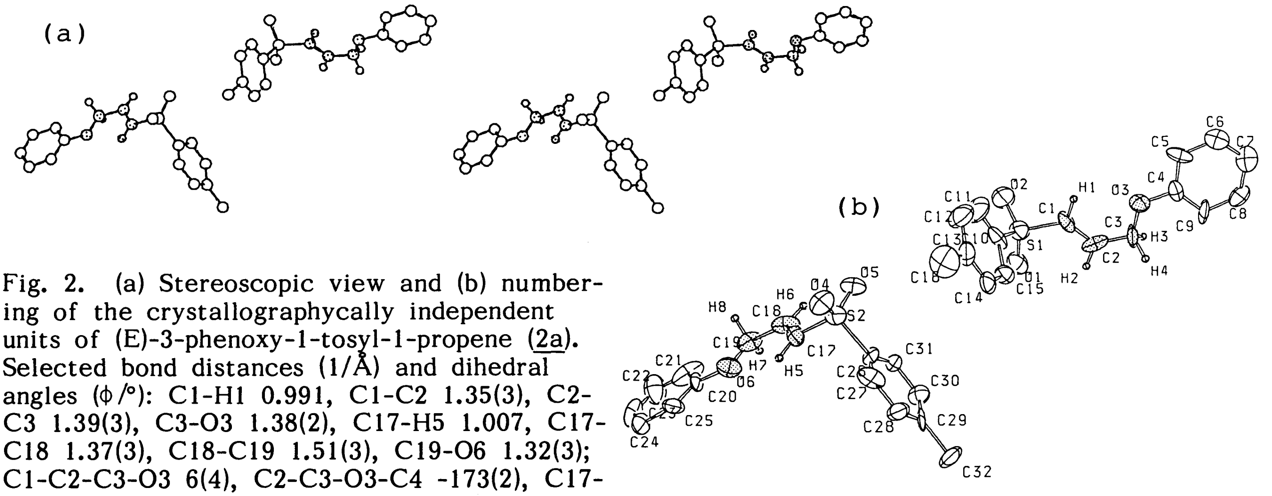


Fig. 2. (a) Stereoscopic view and (b) numbering of the crystallographycally independent units of (E)-3-phenoxy-1-tosyl-1-propene (2a). Selected bond distances (l/Å) and dihedral angles (ϕ/°): C1-H1 0.991, C1-C2 1.35(3), C2-C3 1.39(3), C3-O3 1.38(2), C17-H5 1.007, C17-C18 1.37(3), C18-C19 1.51(3), C19-O6 1.32(3); C1-C2-C3-O3 6(4), C2-C3-O3-C4 -173(2), C17-C18-C19-O6 -1(3), C18-C19-O6-C20 178(2).

room temperature. Fortunately, (E)-3-tosyl-2-propenal ethylene acetal (4) similar to 2b gave the single crystal suitable for X-ray analysis (Fig. 3).$^{5)}$ Once again it was found that 4 has syn-conformation (O4-C8 2.788(5) Å, O4-H8 2.56(4) Å) in spite of the lack of p-orbital on the oxygen atom (O4). Ultimately, the syn-conformation of 2a,b, the origin of "syn-effect" observed in the conversion of the (E)-vinyl sulfones to the corresponding allyl sulfones with DBU, cannot be ascribed to 6π-electron homoaromaticity but intramolecular hydrogen bonding or dipole-dipole interaction.

However, the question why the "syn-effect" was observed for (E)-vinyl sulfones such as 1 having no phenoxy or alkoxy group on γ-position remains. Therefore, X-ray crystallography of the terminal olefin (5) having 2-naphthalenesulfonyl group as a crystallizing auxiliary was performed (Fig. 4).$^{6)}$ The syn-conformation was surprisingly observed (C13-C16 2.94(1) Å, C13-H17 2.67(10) Å, C16-H12 2.87(5) Å, C16-H13 2.93(4) Å) again, contrary to the reported preferable structure of 1-butene, CH_3-skew (83% of rotamer population).$^{7)}$ Although the structure of 5 is only of the solid state [its packing diagram is shown in Fig. 4(c)] till now, it is very suggestive regarding the syn-conformation of the olefinic compounds. Related works including the structure of 5 in solution are further in progress in our laboratory.

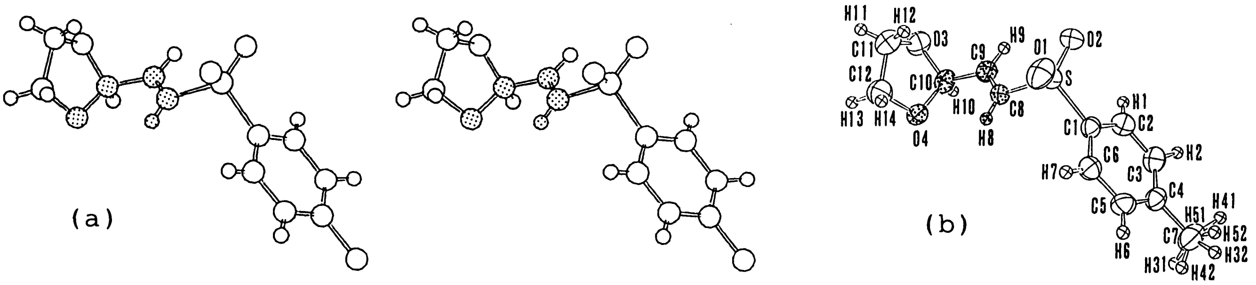


Fig. 3. (a) Stereoscopic view and (b) numbering of (E)-3-tosyl-2-propenal ethylene acetal (4). Selected bond distances (l/Å) and dihedral angles (ϕ/°): C8-H8 0.85(4), C8-C9 1.302(6), C9-C10 1.500(6), C10-O3 1.405(5), C10-O4 1.406(5); C8-C9-C10-O4 5.1(6), C9-C10-O4-C12 97.9(4). The methyl group centered at C7 suffered from twofold disorder with half occupancy for two sets of hydrogen atoms.

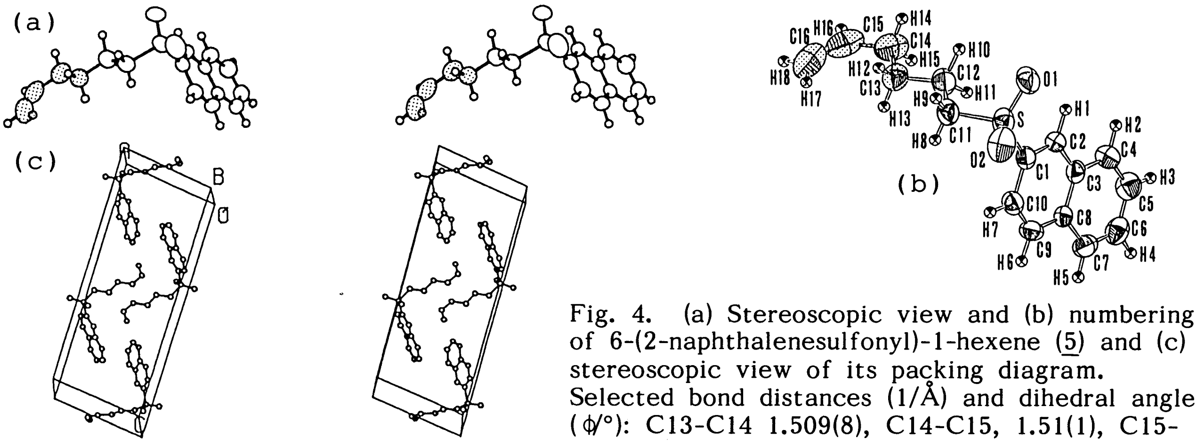


Fig. 4. (a) Stereoscopic view and (b) numbering of 6-(2-naphthalenesulfonyl)-1-hexene (5) and (c) stereoscopic view of its packing diagram. Selected bond distances (l/Å) and dihedral angles (φ/°): C13-C14 1.509(8), C14-C15, 1.51(1), C15-C16 1.27(1), C16-H18 1.00(7); C12-C13-C14-C15 174.8(5), C13-C14-C15-C16 5(1).

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4) 2a, Mp 70 °C (from i-PrOH). Crystal data: $C_{16}H_{16}O_3S$, FW=288.4, Z=8, monoclinic, space group $P2_1/n$, a=16.630(4), b=7.669(2), c=24.046(7) Å, β=92.88(2) °, U=3063(2) $Å^3$, Dc=1.25 g/cm^3, F(000)=1216, μ(Mo-Kα)=2.15 cm^{-1}. Intensities were measured on a Rigaku AFC-5R diffractometer using Mo-Kα radiation within 2θ=45 ° and θ-2θ scan method. Observed independent reflections of 982 with I>3σ(I) were used in the structure analysis and refinement applying TEXSAN program system. The final R factor was 0.070.

5) 4, Mp 107 °C (from i-PrOH). This compound could not be converted to the allylsulfone by treatment with DBU, probably due to the unstable ketene acetal structure of the product. Crystal data: $C_{12}H_{14}O_4S$, FW=254.3, Z=2, monoclinic, space group $P2_1$, a=5.489(1), b=7.824(2), c=13.877(2) Å, β=90.95(1) °, U=595.8(2) $Å^3$, Dc=1.42 g/cm^3, F(000)=268, μ(Mo-Kα)=2.71 cm^{-1}; Rigaku AFC-5R, 2θ=55 °, θ-2θ scan method, number of observation=1077 (I>3σ(I)), TEXSAN program system, R=0.034.

6) 5, Mp 70.5-71.0 °C (from EtOH/H_2O). Crystal data: $C_{16}H_{18}O_2S$, FW=274.4, Z=4, monoclinic, space group $P2_1/c$, a=9.817(4), b=5.770(6), c=25.97(1) Å, β=100.34(3) °, U=1447(2) $Å^3$, Dc=1.26 g/cm^3, F(000)=584, μ(Mo-Kα)=2.09 cm^{-1}; Rigaku AFC-5R, 2θ=55 °, θ-2θ scan method, number of observation=1309 (I>3σ(I)), TEXSAN program system, R=0.049.

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