The Addition of 2,4-Dinitrobenzenesulfenyl Chloride to *cis*- and *trans*-1-Arylpropenes and Some Other Olefins

Kunisuke IZAWA, Tadashi OKUYAMA, and Takayuki FUENO

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560

(Received November 5, 1973)

Kinetic investigations were carried out on the addition of 2,4-dinitrobenzenesulfenyl chloride to the geometrically isomeric pairs of various 1-arylpropenes as well as some related olefins. All the *trans* isomers of 1-arylpropenes were more reactive than the corresponding *cis* isomers and the Hammett correlations were observed for respective isomers with $\rho = -2.64$ (*trans*) and -2.3 (*cis*). By contrast, *cis*-alkenes were more than 10 times as reactive as the corresponding *trans* isomers. The reactivities of various unsaturated compounds in this reaction were found to be correlated with their ionization potentials constituting two lines accodring to the type of substrates. It was concluded that the greater reactivity of *trans*-1-arylpropene as compared with the *cis* isomer is ascribable to the difference in the charge-transfer interaction between the electrophile and a substrate at the transition state. The conclusion is contrasting to the generalization that the relative *cis*/*trans* reactivity of alkenes is determined mainly by the Coulombic interaction at the transition state.

The addition of sulfenyl halide to olefins is known to proceed through an episulfonium ion intermediate.[1] The influence of electronic effects on the rate of this reaction has been extensively studied with various olefins; ring-substituted styrenes,[2] cyclic olefins,[3-5] and alkenes.[6,7] However, little attention has ever been paid to the relative reactivities of geometrical isomers. Available data seem to suggest complexity of the reactivity.

cis-Alkene was found to react faster than the *trans* isomer[7] and the latter deviates from the Hammett-Taft correlation.[6] *cis*-Stilbene, on the other hand, is less reactive than *trans*-stilbene; this observation was explained in terms of the steric effects against electrophilic attack to the former.[8]

In the present study, we have investigated the reaction of 2,4-dinitrobenzenesulfenyl chloride (**1**) with *cis*- and *trans*-1-phenylpropenes (**2c** and **2t**) and their ring-substituted derivatives, *cis*- and *trans*-2-heptenes (**3c** and **3t**) and *cis*- and *trans*-4-methyl-2-pentenes (**4c** and **4t**) in order to clarify the relationship between relative *cis*/*trans* reactivities and olefin structure. The reaction rates of some other related olefins have been measured for the sake of comparison. Possible factors that influence these reactivities have been discussed.

Results

Reaction Products. The reaction of **1** with **2t** in glacial acetic acid led to a high yield of 1 : 1 adduct which was shown to be *erythro*-1-phenyl-1-chloro-2-(2,4-dinitrophenylthio)propane by NMR specroscopy. That is, the addition is specifically of Markownikoff-type and *anti* fashion. On the other hand, the reaction with **2c** under the same conditions yielded *ca.* 30% of the anti-Markownikoff isomer together with 70% the normal adduct. Both adducts were *threo*-type; the addition is, therefore, specifically *anti*. Stereochemistry of the adducts was determined by comparing the NMR spectra (see Experimental) with the compilation of spectra of related compounds.[9,10]

Kinetic Measurements. The rates of addition of **1** to **2c** and **2t** and their ring-substituted derivatives were determined in dry acetic acid solution. The reactions were followed by measuring the rates of disappearance of the sulfenyl chloride by the titration method. The rate is first order in each reactant as was found for other olefins.[2-6] Initial reactant concentrations were varied in the different rate runs but there was found no indication of deviations from the simple second-order kinetics.

The second-order rate constants k_2 for phenylpropene derivatives are summarized in Table 1. All the *trans* isomers of phenylpropenes are several times more reactive than the corresponding *cis* isomers. From the temperature dependence of k_2, activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, were calculated in a usual way. Although they may not be precise enough because of a limited range of temperature variation, they are included in Table 1 for the sake of comparison between *cis*-*trans* isomeric pairs.

The Hammett $\rho\sigma$ correlation for the reaction of the derivatives of **2c** and **2t** at 25 °C are shown in Fig. 1. The reaction constants ρ were evaluated excluding *p*-methoxy derivatives, which show apparent

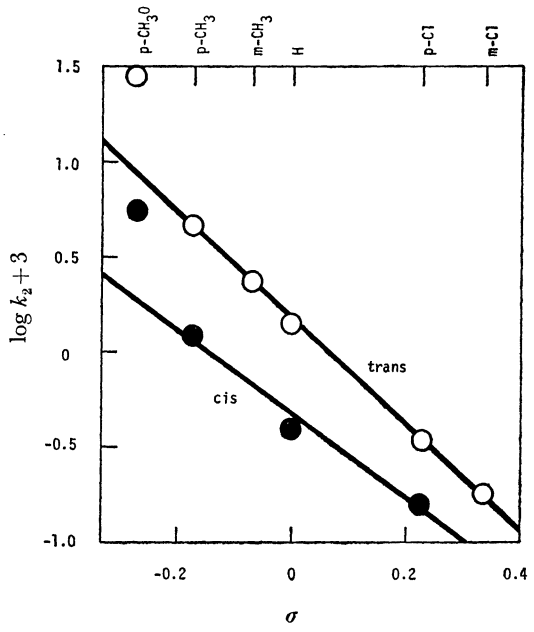

Fig. 1. The Hammett plots for the reaction of **1** with **2t** (○) and **2c** (●) in acetic acid at 25 °C.

Table 1. Second-order rate constants and activation parameters for the reaction of **1** with ring-substituted 1-phenylpropenes in acetic acid

Substituent	$10^3 k_2$, $M^{-1} s^{-1}$				$\Delta H^{\neq}$, kcal/mol	$\Delta S^{\neq}$, e. u.
	15 °C	25 °C	35 °C	45 °C		
			trans-1-Phenylpropene			
p-CH_3O	16.8	28.8			8.7	−36.9
p-CH_3		4.60	8.20		10.0	−37.2
m-CH_3		2.34				
H(**2t**)		1.44	2.72	5.29	11.7	−32.8
p-Cl		0.335	0.607		10.3	−40.3
m-Cl		0.180				
			cis-1-Phenylpropene			
p-CH_3O	2.48	5.63			13.5	−23.0
p-CH_3		1.25	2.83		15.7	−19.7
H(**2c**)		0.393	1.04	2.79	17.9	−14.4
p-Cl		0.156	0.368		15.2	−25.6

Table 2. Second-order rate constants and activation parameters for the addition of **1** to some olefins

No.	Olefin	$10^3 k_2$, $M^{-1} s^{-1}$				$\Delta H^{\neq}$ kcal/mol	$\Delta S^{\neq}$, e.u.
		18 °C	25 °C	35 °C	45 °C		
5	Styrene[a)]		0.741				
6	Indene		0.512	1.11		13.6	−28.5
7	1-Hexene		1.32	2.49	4.67	11.4	−34.1
3t	*trans*-2-Heptene		1.59	3.03		11.2	−34.1
3c	*cis*-2-Heptene	14.7	18.8			5.5	−47.8
4t	*trans*-4-Methyl-2-pentene		0.457	1.09		15.4	−22.7
4c	*cis*-4-Methyl-2-pentene	20.0	26.9	41.4		7.1	−42.3

a) Orr and Kharasch[2)] reported $0.737 \times 10^{-3} M^{-1} s^{-1}$ for k_2 value at 25 °C.

deviation from the linearities: $\rho = -2.64$ for the *trans* isomers and $\rho \sim -2.3$ for the *cis* isomers.

Listed in Table 2 are the kinetic data for styrene (**5**), indene (**6**) and some alkenes. The *cis* isomer of an alkene is significantly reactive than its *trans* isomer.

Discussion

Specific *anti*-additions of **1** to both **2c** and **2t** are explained as usual by the mechanism involving an episulfonium ion intermediate.[1)] The anti-Markownikoff-type adduct was found only for the *cis* isomer (30 %). This trend was observed earlier in the addition of *p*-chlorobenzenesulfenyl chloride.[10)] In this reaction, **2c** gave 66% of anti-Markownikoff product. The reduced yield of anti-Markownikoff product in the present reaction is consistent with the general observation[11)] that the *ortho*-nitro substitution of sulfenyl chloride tends to increase Markownikoff adduct.

The *trans* isomers of aryl-substituted olefins were found to be more reactive than the *cis* counterparts, while *trans*-alkenes were found to be less reactive than the *cis* isomers. These results are seemingly similar to those obtained for the protonation in which *cis* isomers are more reactive in the case of aliphatic olefins but are less reactive in the case of most of 1-phenylpropene derivatives.[12)]

However, the effect of ring substituents on the protonation rate of **2** is contrasting to the present results. In the hydrochlorination of **2**, the relative *cis*/*trans* reactivity increases with increasing electron-donating character of the ring substituent. That is, the ring substitution exerts more influence on the reactivity of the *cis* isomer ($|\rho_{cis}| > |\rho_{trans}|$).[12)] From these observations, the reduced reactivity of the *cis* isomers was interpreted by the steric inhibition of intermediate solvation.[12)] On the other hand, the substituent effects observed in the present reaction are just opposite to those observed in the hydrochlorination. The relative *cis*/*trans* reactivity tends to diminish with the increasing electron-donating character of ring substituents. Correspondingly, the magnitude of the reaction constant ρ is greater for the *trans* isomers than for the *cis* isomers (Fig. 1). Furthermore, all the values of $\Delta H^{\neq}$ are greater for the *cis* isomers. These results seem to suggest, in contrast to the hydrochlorination, that the *trans* isomers are electronically more reactive in sulfenylation of 1-phenylpropenes. If the steric factor were important to the reaction,[13)] its effect would be analogous to that in the hydrochlorination.[12)]

Electronic interactions controlling the reactivity may divided into two factors, Coulombic and charge-transfer interactions.[14,15)] It was concluded that the former predominates in the greater reactivity of *cis* isomers in protonation.[13,14)] The latter factor of charge transfer interaction seems to contribute to the greater

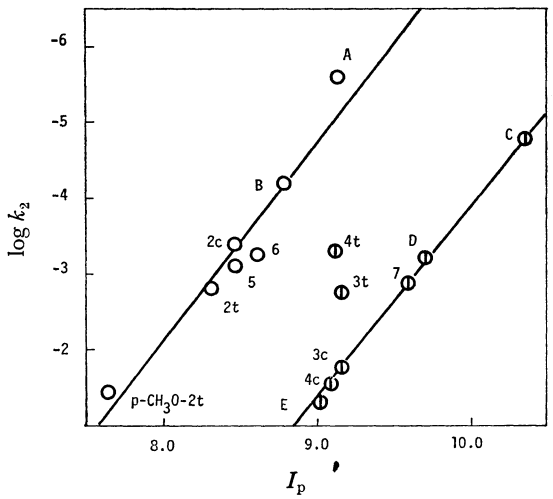

Fig. 2. Correlation of the reaction rates (k_2 for the addition of **1** in acetic acid at 25 °C) with ionization potentials. Ionization potential data are taken from Y. Morino, *et al.*, "Kagaku Binran (Handbook of Chemistry)" Ed. by Chem. Soc. Japan, Maruzen, Tokyo, 1966 and K. Yamaguchi, Doctor thesis, Osaka Univ., 1972. For Nos., see Tables 1 and 2. (A) Phenylacetylene (Ref. 8); (B) 1-phenylpropyne; (C) 1-hexyne; (D) 2-heptyne (T. Okuyama, K. Izawa, and T. Fueno, *J. Org. Chem.*, **39**, 351 (1974)); (E) cyclohexene (Ref. 4).

reactivity of the *trans* isomers in the present reaction. Importance of the charge transfer interaction is in accord with the tendency of episulfonium intermediate formation.

The charge-transfer controlled reactivity might be ascribed to the softness of electrophilic sulfur. The correlation between the reactivity of an olefin or an acetylene and its ionization potential (I_p) is substantiated in Fig. 2 as expected for the charge-transfer controlled reaction. Two classes of compounds, aromatic and aliphatic, constitute different lines. This fact might arise from the different contributions from other factors to the respective class of unsaturated compounds.

The greater reactivity of **2t** seems to reflect the lower ionization potential of **2t** as compared with **2c**. The large magnitude of the ρ value for the *trans* isomers compared with that for the *cis* isomers is consistent with the greater contribution of charge-transfer interaction to the reactivities of the former.

As for the alkene series, the difference in ionization potential is negligibly small between *cis* and *trans* isomers. Thus, the reactivity difference does not seem to reflect charge-transfer contribution. The reduced reactivity of the *trans* isomers as compared with the *cis* counterparts will be accounted for in terms of different Coulombic interaction as in the case of protonation.

The observed Hammett-Taft correlation for sulfenyl chloride addition to alkenes[6] may have some bearing on this log k_2—I_p correlation. The rate enhancement by *cis*-β-methyl substitution corresponds to the decrease in I_p (**7** and **3c**). The points for the *trans*-alkenes (**3t** and **4t**) are deviated from the line in Fig. 2. This type of deviations of *trans*-alkenes were pointed out also in the Hammett-Taft correlations not only for sulfenylation[6] but bromination.[16]

In conclusion, the contribution of charge-transfer interaction is considerably great in the reaction of "soft" reagent like sulfur with a substrate of low I_p even if the reaction is ionic. Relative *cis*/*trans* reactivities of aromatic olefins are ascribed to this factor.

Experimental

All boiling points and melting points are uncorrected. The nuclear magnetic resonance spectra were obtained on a JNM-4H-100 spectrometer operating at a frequency of 100 MHz. All vpc analyses were performed with a Shimadzu gas chromatograph Model 4APT.

Materials. Glacial acetic acid was dried according to the literature.[17] 2,4-Dinitrobenzenesulfenyl chloride (**1**) was prepared by the method of Kharasch and Langford[18] and recrystallized from carbon tetrachloride; mp 95.0—95.5 °C (lit,[18] 95.0—95.5 °C).

trans-1-Phenylpropene (**2t**) and its ring-substituted derivatives were prepared by prototropic rearrangement[19] of corresponding allylbenzenes, which were obtained by the Grignard coupling between allylbromide and bromobenzenes.[20] *cis*-1-Phenylpropene (**2c**) and its ring-substituted derivatives were prepared by decarboxylation of corresponding α-methylcinnamic acids, which were obtained by the Perkin reaction of appropriate benzaldehydes.[21] All the 1-phenylpropenes obtained were geometrically pure over 95% and were further purified by preparative vpc whenever necessary. The isomer thus purified were pure in >99%. IR spectra of **2t** and **2c** agreed well with those reported in the literature. Their boiling points and spectral data were as follows: **2t**, bp 48 °C(8 mmHg) (lit,[22] 105 °C (80 mmHg)); NMR (CCl_4) δ 1.84 (3H, d, J=6 Hz, CH_3), 5.96—6.40 (2H, m, -CH=CH-) 7.07—7.73 (5H, C_6H_5). *p*-CH_3O-**2t**, bp 108 °C (12 mmHg); NMR (CCl_4) δ 1.83 (3H, d, J=6 Hz, CH_3), 3.67 (3H, s, OCH_3), 5.8—6.33 (2H, m, -CH=CH-), 6.61—7.15 (4H, C_6H_4). *p*-CH_3-**2t**, bp 58 °C (4 mmHg); NMR (CCl_4) δ 1.83 (3H, d, J=6 Hz, CH_3), 2.27 (3H, s, CH_3), 5.85—6.37 (2H, m, -CH=CH-), 6.9—7.13 (4H, C_6H_4). *m*-CH_3-**2t**, bp 67 °C (8 mmHg); NMR (CCl_4) δ 1.85 (3H, d, J=6 Hz, CH_3) 2.30 (3H, s, CH_3), 5.95—6.38 (2H, m, -CH=CH-), 6.85—7.07 (4H, C_6H_4). *p*-Cl-**2t**, bp 79 °C (7 mmHg); NMR (CCl_4) δ 1.84 (3H, d, J=6 Hz, CH_3), 5.95—6.36 (2H, m, -CH=CH-), ~7.15 (4H, C_6H_4). *m*-Cl-**2t**, bp 80.5 °C (7 mmHg); NMR (CCl_4) δ 1.86 (3H, d, J=7 Hz, CH_3), 5.96—6.40 (2H, m, -CH=CH-), 7.05-7.15 (4H, C_6H_4). **2c**, bp 45°C (10 mmHg) (lit,[22] 95—96 °C (80 mmHg); NMR (CCl_4) δ 1.85 (3H, dd, J=7 and 1.5 Hz, CH_3), 5.5—5.85 (1H, m, =CH-Me), 6.85 (1H, dd, J=11 and 1.5 Hz, Ph-CH=), 7.1—7.2 (5H, C_6H_5). *p*-CH_3O-**2c**, bp 88 °C (10 mmHg); NMR (CCl_4) δ 1.85 (3H, dd, J=7 and 1.5 Hz, CH_3), 3.72 (3H, s, OCH_3), 5.42—5.75 (1H, m, =CH-Me), 6.29 (1H, dd, H=11 and 1.5 Hz, Ph-CH=), 6.67—7.20 (4H, C_6H_4). *p*-CH_3-**2c**, bp 66 °C (10 mmHg); NMR (CCl_4) δ 1.84 (3H, dd, J=7 and 1.5 Hz, CH_3), 2.30 (3H, s, CH_3), 5.45—5.80 (1H, m, =CH-Me), 6.83 (1H, dd, J=11 and 1.5 Hz, Ph-Ch-), ~7.06 (4H, C_6H_4). *p*-Cl-**2c**, bp 72 °C (8 mmHg); NMR (CCl_4) δ 1.84 (3H, dd, J=7 and 1.5 Hz, CH_3), 5.5—5.85 (1H, m, =CH-Me), 6.35 (1H, dd, J=11 and 1.5 Hz, Ph-CH=), 7.1—7.2 (4H, C_6H_4).

Styrene (**5**), indene (**6**), 1-hexene (**7**), *trans*- and *cis*-2-heptenes (**3t** and **3c**), and *trans*- and *cis*-4-methyl-2-pentenes

(**4t** and **4c**) were commercially obtained (Nakarai Chemicals) and distilled under nitrogen atmosphere immediately before use.

*Reaction of **1** with **2t**.* A sample of 2.50 g of **1** was mixed with 1.75 g of **2t** in 50 ml dry acetic acid and allowed to react for two days at room temperature. Yellow precipitates were separated and recrystallized from absolute alcohol to give 3.14 g of yellow prisms, mp 91° (83.5% yield as a 1 : 1 adduct). Found: C, 51.34; H, 3.57; N, 7.94; Cl, 9.94; S, 9.14. Calcd for $C_{15}H_{13}O_4N_2ClS$: C, 51.06; H, 3.72; N, 7.95; Cl, 10.06; S, 9.09. NMR ($CDCl_3$) δ 1.63 (3H, d, J=7 Hz, CH_3), 3.95 (1H, double quartet, J=7 and 8 Hz, S-CH-Me), 5.0 (1H, d, J=8 Hz, Ph-CH-Cl), 7.17—7.36 (5H, m, C_6H_5), 7.5—8.78 (3H, m, $C_6H_3(NO_2)_2$). By comparing the spectrum with those of related compounds,[9,10] the adduct was assigned to be *erythro*-1-phenyl-1-chloro-2-(2,4-dinitrophenylthio)propane.

*Reaction of **1** with **2c**.* The reaction product was obtained in the same way as in the case of **2t**. One to one adducts were isolated in *ca.* 80% yield. NMR spectrum in $CDCl_3$ showed that the product is a mixture of isomers. Two doublet signals were observed at δ=1.47 and 1.71 in an integral ratio of 7 : 3. They were attributed to the methyl groups of the *thero*-Markownikoff (δ 1.47) and the *threo*-anti-Markownikoff (δ=1.71) adducts, respectively.

Separation of isomers was carried out by liquid chromatography with silica gel column using ethanol as eluent. The Markownikoff adduct was obtained in 65% yield as yellow needles melting at 113.5 °C. Found: C, 50.95; H, 3.54; N, 8.03; Cl, 9.90; S, 9.18%. Calcd for $C_{15}H_{11}O_4N_2ClS$: C, 50.99; H, 3.68; N, 7.93; Cl, 10.21; S, 9.08%. NMR ($CDCl_3$) δ 1.47 (3H, d, J=6 Hz, CH_3), 4.10 (1H, m, Me-CH) 5.09 (1H, d, J=5 Hz, CHCl), ~7.40 (5H, m, C_6H_5), 7.56 (1H, d, J=8 Hz, 6-H of $C_6H_3(NO_2)_2$), 8.32 (1H, dd, J=8 and 2 Hz, 5-H of $C_6H_3(NO_2)_2$), 8.97 (1H, d, J=2 Hz, 3-H of $C_6H_3(NO_2)_2$).

Kinetic Measurements were made by essentially the same method as used by Orr and Kharasch.[2] Stock solutions of **1** and unsaturated compounds were respectively prepared by dissolving weighed amounts of freshly purified materials in the desired volume of dry acetic acid at the temperature of each run.

References

1) For reviews, see (a) P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems", Elsevier, New York, N. Y. (1966), pp. 166—173; (b) N. Kharasch, "Organic Sulfur Compounds," Vol. 1, Pergamon Press, New York, N. Y., 1961, pp. 375—396; (c) N. Kharasch, Z. S. Ariyan, and A. J. Havlik, *Quart. Rep. Sulfur Chem.*, **1**, 93 (1966); (d) D. R. Hogg and J. H. Smith, *ibid.*, **3**, 63 (1968); (e) R. C. Fahey, *Top. Stereochem.*, **3**, 318 (1968); (f) W. H. Mueller, *Angew. Chem. Int. Ed. Eng.*, **8**, 482 (1969).

2) W. L. Orr and N. Kharasch, *J. Amer. Chem. Soc.*, **78**, 1201 (1956).

3) H. Kwart and L. J. Miller, *ibid.*, **83**, 4552 (1961).

4) C. Brown and D. R. Hogg, *J. Chem. Soc. B*, 1262 (1968).

5) C. Brown and D. R. Hogg, *ibid.*, **1969**, 1054.

6) G. M. Beverly and D. R. Hogg, *ibid.*, **1971**, 175.

7) W. A. Thaler, *J. Org. Chem.*, **34**, 871 (1969).

8) N. Kharasch and C. N. Yiannios, *ibid.*, **29**, 1190 (1964).

9) G. H. Schmid, *Can. J. Chem.*, **46**, 3415 (1968).

10) G. H. Schmid and V. Csizmadia, *Chem. Ind.* (London), **1968**, 1811.

11) G. M. Beverly, D. R. Hogg, and J. H. Smith, *ibid.*, 1403 (1968).

12) K. Izawa, T. Okuyama, and T. Fueno, This Bulletin, the preceding paper.

13) A slightly reduced reactivity of **2c** as compared with styrene seems to reflect the steric effects arising from a non-planar *cis* structure of **2c**, even though the effects are too small to offset the relative reactivity to **2c**.

14) K. Yamaguchi, T. Okuyama, and T. Fueno, to be published.

15) G. Klopman, *J. Amer. Chem. Soc.*, **90**, 223 (1968).

16) J. E. Dubois and G. Mouvier, *Tetrahedron Lett.*, **1965**, 1629; **1963**, 1325.

17) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath & Co., Boston, Mass. (1955).

18) N. Kharasch and R. B. Langford, "Organic Syntheses," Vol. 44, p. 47 (1964).

19) A. Schriesheim, C. A. Rowe, Jr., and L. Naslund, *J. Amer. Chem. Soc.*, **85**, 2111 (1963).

20) E. B. Hershberg, *Helv. Chim. Acta*, **17**, 352 (1934).

21) J. R. Johnson, "Organic Reactions," Vol. 1, ed. by R. Adams *et al.*, John Wiley & Sons, Inc., New York and London (1942), p. 251.

22) M. J. S. Dewar and R. C. Fahey, *J. Amer. Chem. Soc.*, **85**, 3645 (1963).