Demonstration of the Intramolecular Character of the O,N-Acyl Transfer Reaction of 1 → 2. Solutions of **1** (X = H) in dimethyl sulfoxide-d_6 were prepared at concentrations of 0.029 M and 0.21 M. The acetyl hydrogens and the aromatic 3-hydrogen were monitored to obtain rate constants of 0.35 h^{-1} and 0.43 h^{-1}, respectively, establishing that within the error limits of the measurements, the rate constant is concentration-independent.

Estimation of Atomic Distances in the Transition-State Model. The following bond lengths were obtained from diffraction data for LL-cystine:[12] S–S, 2.038; C–S, 1.816; C–C, 1.525; N–C, 1.484. The N–C and C–O bond lengths to the acyl carbon of the transition state were assumed to be 1.49 and 1.43 Å, respectively. Bond angles were obtained from the LL-cystine structure[12] as shown in **13**. A simple recursive distance-calculating program without energy minimization was written and used to obtain the O–S_2 distance for **17**. The O–S distance for **3** was calculated from X-ray data for dibenzofuran.[25]

Acknowledgment. Financial support from NIH Grant GM 15453 is gratefully acknowledged. We thank Dr. C. Costello of Prof. K. Biemann's laboratory for high resolution and field desorption mass spectra.

(25) Banerjee, A. *Acta Crystallogr., Sect. B* **1973**, *29*, 2070.

Registry No. **1** (X = Z = H, R = Me, Y = OMe), 101762-06-5; **1** (X = Z = H, R = Me, Y = OMe, free base), 84288-41-5; **2** (X = Z = H, R = Me, Y = OMe), 101774-00-9; **2** (X = Cl, Z = H, R = Me, Y = OMe), 101762-37-2; **3**, 101697-54-5; **4**, 101762-07-6; **5**, 63012-07-7; **6**, 101762-08-7; **7**, 101762-09-8; **8**, 101762-10-1; **9**, 101762-11-2; **10**, 101762-12-3; **19b** (*NH*→*N*-Boc), 101762-13-4; **22a**, 101697-58-9; **22b**, 101762-14-5; **22c**, 101697-56-7; **23a**, 101762-15-6; **23b**, 101762-16-7; **23c**, 101762-17-8; **24a**, 101762-18-9; **24b**, 101762-19-0; **24c**, 101762-20-3; **25a**, 101762-21-4; **25c**, 101762-22-5; **26a**, 101762-23-6; **26c**, 101762-24-7; **27a**, 101762-25-8; **27c**, 101762-26-9; **28b**, 101762-27-0; **29b**, 101762-28-1; **29c**, 101762-29-2; **30a**, 51596-34-0; **30c**, 101762-30-5; **31a**, 51596-35-1; **31c**, 101762-31-6; **32a**, 101762-32-7; **32c**, 101762-33-8; **33b**, 101762-34-9; **34b**, 101762-35-0; **34c**, 101774-01-0; **35b**, 101762-36-1; **36c**, 101774-02-1; Me_3SiCl, 75-77-4; 2-bromodibenzofuran, 86-76-0; 4-bromodibenzofuran, 89827-45-2; 4-methoxydibenzofuran, 41799-27-3; 4-methoxy-6-(trimethylsilyl)dibenzofuran, 101762-38-3; 4-(trimethylsilyl)-6-methoxyphenoxythiin, 101762-39-4; 6-deuterio-4-methoxyphenoxythiin, 101762-40-7; 4-acetoxyphenoxythiin, 101762-41-8; 4-hydroxy-6-(methoxycarbonyldithio)phenoxythiin, 101762-42-9; 4-acetoxy-6-(methoxycarbonyldithio)phenoxythiin, 101762-43-0; *N*-benzyloxycarbonyl-L-alanine, 1142-20-7; 4-hydroxydibenzofuran, 19261-06-41; 1-chloro-4-hydroxydibenzofuran, 41799-31-9; methyl *N*-(*tert*-butoxycarbonyl)-*S*-(methoxycarbonylsulfenyl)-L-cysteinate, 53907-23-6; methoxycarbonylsulfenyl chloride, 26555-40-8.

Phenonium Ion in [3.*n*]Paracyclophanes. Effects of Neighboring Groups, Steric Size of Substituents, and Strain on Solvolysis Reactions

Jun Nishimura,* Yukihiro Okada, and Akira Oku

Department of Chemistry, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan

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The effects of steric hindrance, of strain on the structure of the phenonium ion, and of the neighboring group have been studied in the solvolyses of some [3.*n*]paracyclophanylmethyl tosylates. The reaction path was affected considerably by the steric hindrance of a methyl group attached to the cyclophane skeleton. The effect of strain on the structure of the phenonium ion was clearly demonstrated in the acetolyses of secondary tosylates. A strong anchimeric assistance to the ionization step by the [3.3]paracyclophanyl group was shown. The acetolysis rate constants of [3.*n*]paracyclophanylmethyl tosylates decreased with increasing methylene chain length. The rate enhancement is attributed to the π–π transannular interaction of the two overlapping benzene nuclei.

Studies of the phenonium ion include reports on substituent effects,[1] solvent effects,[2] strain effects,[3] steric hindrance,[4,5] direct observation by NMR spectroscopy,[6] and through-space participation of one benzene nucleus.[7] We have been interested in how the solvolysis (dynamic) path and rate might be influenced by the through-space interaction of two or more benzene nuclei oriented face-to-face, as in the cyclophanes.

The static interactions of the two benzene nuclei of [2.2]paracyclophane and other cyclophanes have been reported in studies of the acidity of cyclophanecarboxylic acid[8] and donor–acceptor complex formation.[9] Sheehan and Cram[9b] showed that [2.2]paracyclophane, which has the shortest spacing between the benzene nuclei and the deformed benzene rings,[10] is less electron donating than [3.3]paracyclophane. Furthermore, UV spectroscopy[9a] indicates that the nature of [*n*.*n*]paracyclophanes should approach that of the corresponding α,ω-diarylalkanes as *n* increases. Accordingly, [3.3]paracyclophane, which shows the strongest static transannular π–π interaction, should also show strong "π–π through space" effects in solvolysis reactions.

Hedaya and Kyle have studied phenonium ion incorporated in the [2.2]paracyclophane ring system.[11] They

(1) For a review, see: Lancelot, C. J.; Cram, D. J.; Schleyer, P. v. R. *Carbonium Ion*; Olah, G. A., Schleyer, P. v. R., Ed.; Wiley-Interscience: New York, 1972; Vol. III, pp 1347–1483.

(2) Schadt, F. L., III.; Lancelot, C. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1978**, *100*, 228–246, and references cited therein.

(3) (a) Huisgen, R. *Angew. Chem.* **1957**, *69*, 341–359. (b) Huisgen, R.; Seidl, G. *Chem. Ber.* **1963**, 2730–2739. (c) Huisgen, R.; Seidl, G. *Chem. Ber.* **1963**, 2740–2749. (d) Huisgen, R.; Rauenbusch, E.; Seidl, G.; Wimmer, I. *Ann.* **1964**, *671*, 41–57. (e) Huisgen, R.; Seidl, G. *Tetrahedron* **1964**, *20*, 231–241. (f) Huisgen, R.; Seidl, G.; Wimmer, I. *Tetrahedron* **1964**, *20*, 623–631. (g) Seidl, G.; Huisgen, R.; Hill, J. H. M. *Tetrahedron* **1964**, *20*, 633–640. (h) Seidl, G.; Huisgen, R. *Chem. Ber.* **1964**, 249–254.

(4) (a) Cram, D. J.; Singer, L. A. *J. Am. Chem. Soc.* **1963**, *85*, 1075–1079. (b) Cram, D. J.; Harris, F. L., Jr. *J. Am. Chem. Soc.* **1967**, *89*, 4642–4651.

(5) Nugent, M. J.; Vigo, T. L. *J. Am. Chem. Soc.* **1969**, *91*, 5483–5486.

(6) Olah, G. A.; Spear, R. J.; Forsyth, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 6284–6289.

(7) For a review, see: Tanida, H. *Acc. Chem. Res.*, **1968**, *1*, 239–245.

(8) Segel, M. G.; Liotta, C. L.; Cram, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 1387–1391.

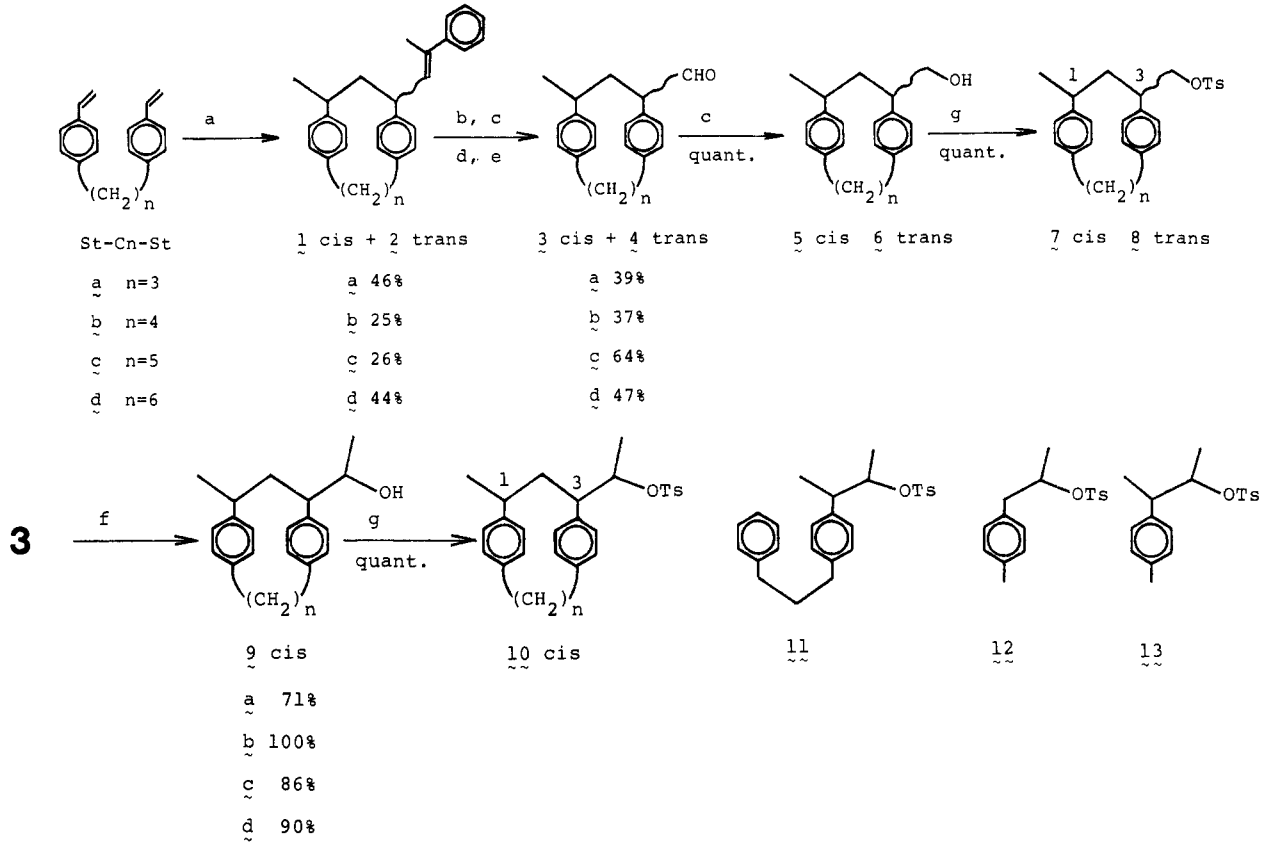
(9) (a) Cram, D. J.; Bauer, R. Y. *J. Am. Chem. Soc.* **1959**, *81*, 5971–5977. (b) Sheehan, M.; Cram, D. J. *J. Am. Chem. Soc.* **1969**, *91*, 3553–3558.

(10) As a review, see: Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* **1971**, *4*, 204–213.

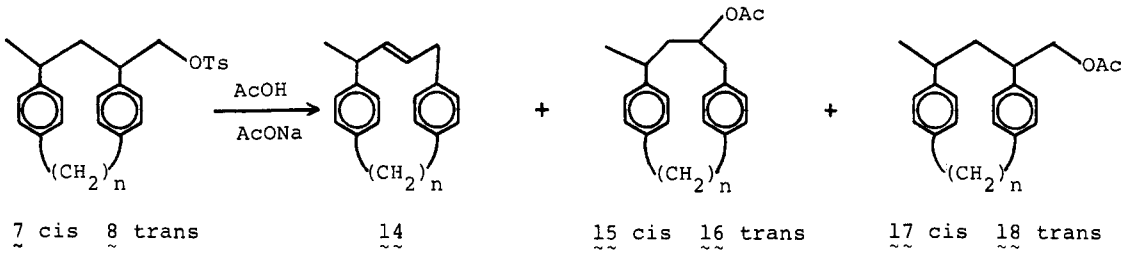
(11) Hedaya, E.; Kyle, L. M. *J. Am. Chem. Soc.* **1966**, *88*, 3667–3669.

0022-3263/86/1951-1838$01.50/0

Scheme I[a]



[a] (a) 2-Phenylpropene, CF_3SO_3H in dry benzene at 50 °C for 20 min; (b) O_3 in CCl_4; (c) $LiAlH_4$ in ether; (d) PCC in CH_2Cl_2; (e) SiO_2 column chromatography; (f) MeMgI in ether; (g) TsCl in pyridine at 0–25 °C.



(1)

found a rather small effect of the high strain of [2.2]-paracyclophane (34 kcal/mol)[12] by kinetic data and ascribed it to the fact that the [2.2]paracyclophane system does not attain favorable geometry for phenonium ion formation in the transition state.

We have reported a new cationic cyclocodimerization route to [3.n]paracyclophane derivatives,[13] so that we were prompted to investigate the phenonium ions generated in a series of cyclophane skeletons. By using homologous [3.n]paracyclophane skeletons, one can systematically change strain, steric hindrance, and electronic effects to see how these effects impinge on solvolysis rates. Moreover, our cyclophanes have a methyl group attached to the three-carbon bridge, so that the stereochemical course of solvolysis reactions is conveniently determined.

Results and Discussion

1. Preparation of Materials. The cyclophanylmethyl tosylates *cis*-**7**, *trans*-**8**, and *cis*-**10** were conveniently prepared by our method (Scheme I).[13] The cis–trans notation in this paper describes the relationship between methyl group at C-1 of the three-carbon bridge and a substituent at C-3 of that bridge. Other tosylates were obtained from the corresponding alcohols as reported.[14]

Cis aldehydes **3** were treated with MeMgI to afford cis-secondary alcohols **9**, which were all ~4:1 mixtures of threo and erythro diastereomers. The major alcohol was assigned the threo structure in accordance with Cram's rule[15] and ^1H NMR spectroscopic evidence. Since these diastereomers could not be separated, we used the isomer mixtures for further study.

The tosylation of primary and secondary alcohols **5**, **6**, and **9** proceeded smoothly in pyridine at 0–25 °C. The tosylates used for solvolysis studies were shown to be up to 95% pure by ^1H NMR (200 MHz).

2. Product Analysis. Tosylates **7**, **8**, and **10** were acetolyzed in 0.05 M sodium acetate buffered acetic acid under reflux. Tosylates **7** and **8** gave olefins **14**, rearranged

(12) (a) Boyd, R. H. *Tetrahedron* **1966**, *22*, 119–122. (b) Boyd, R. H. *J. Chem. Phys.* **1968**, *49*, 2574–2583. (c) Shieh, C.; McNally, D. C.; Boyd, R. H. *Tetrahedron* **1969**, *25*, 3653–3665.

(13) Nishimura, J.; Hashimoto, K.; Okuda, T.; Hayami, H.; Mukai, Y.; Oku, A. *J. Am. Chem. Soc.* **1983**, *105*, 4758–4767.

(14) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; John Wiley and Sons: New York, 1967; Vol. 1, p 1180.

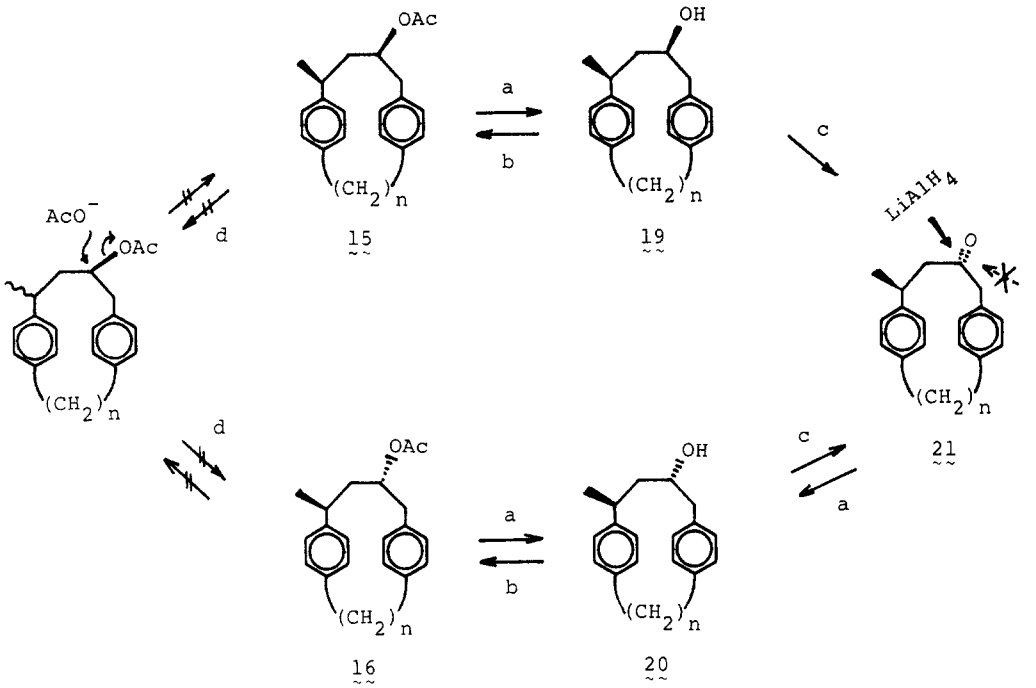
(15) Cram, D. J.; Elhafez, F. A. A. *J. Am. Chem. Soc.* **1952**, *74*, 5828–5835.

Table I. Product Distribution in Acetolysis of Tosylates[a]

tosylate[b]	product yield, %			
	olefin	rearranged acetate[b]	unrearranged acetate	total yield
7a/8a (100:0)	**14a**, 5	**15a/16a** (85:15), 88	**17a**, 1	94
7a/8a (1:99)	**14a**, 2	**15a/16a** (2:98), 94	**18a**, 3	99
7b/8b (100:0)	**14b**, 13	**15b/16b** (96:4), 68	**17b**, 8	89
7b/8b (6:94)	**14b**, 13	**15b/16b** (5:95), 75	**18b**, 6	94
7c/8c (98:2)	**14c**, 36	**15c/16c** (92:8), 47	**17c**, 9	92
7c/8c (0:100)	**14c**, 32	**15c/16c** (0:100), 63	**18c**, 5	100
7d/8d (100:0)	**14d**, 40	**15d/16d** (81:19), 52	**17d**, 0	92
7d/8d (6:94)	**14d**, 43	**15d/16d** (6:94), 47	**18d**, 3	93
10a	**25a**, 4	**26a**, 85	**27a**, 0	89
10b	**25b**, 11	**26b**, 60	**27b**, 21	92
10c	**25c**, 27	**26c**, 35	**27c**, 33	95
10d	**25d**, 10	**26d**, 0	**27d**, 79	89

[a] Reaction conditions: tosylate (ca. 1 mM) in 0.05 M NaOAc–buffered acetic acid under reflux for 1 day. [b] Isomer ratios are given in parentheses.

Scheme II[a]



[a] (a) $LiAlH_4$, ether; (b) AcCl, pyridine; (c) PCC, CH_2Cl_2; (d) AcOH–AcONa, reflux.

acetates **15** and/or **16**, and unrearranged acetates **17** and **18**, respectively (eq 1). Product distributions are summarized in Table I. Olefins **14** contain an unconjugated trans double bond and appear to have been formed through phenonium ion intermediates. The proportion of olefins **14** produced increased with decreasing strain of the cyclophane system that contains the trans double bond.[16]

The rearranged acetates **15** and **16** were not isomerized under the reaction conditions, as shown in Scheme II. Cis and trans acetates **15** and **16** were deacetylated by $LiAlH_4$ followed by oxidation with pyridinium chlorochromate (PCC) to give the corresponding ketones **21**. It is interesting to note that the reduction of the ketones **21** with $LiAlH_4$ gave exclusively trans alcohols **20**. This selectivity is attributed to the predominance of the ketone conformer with a quasi-equatorial methyl group, which is attacked by the metal hydride from the open side.

The cis tosylate **7** gave cis and trans acetates **15** and **16**, whereas the trans tosylate **8** afforded exclusively trans acetate **16**.[17] These results suggest that **7** and **8** underwent rearrangement via internal return to form **22** and **23** in this acetolysis. Tosylate **22** has a quasi-equatorial methyl group, and acetate anion can attack it from a quasi-axial direction to give acetate **16** in a k'_s process (see Scheme III). In fact, when **22a** and **22d** were acetolyzed, they gave considerable amounts of **16a** and **16d**, respectively (vide infra). On the other hand, tosylates **23** have methyl groups in quasi-axial positions, which hinders the attack of solvent from the quasi-axial side. If the coplanar phenonium ion **24** with a quasi-equatorial methyl group were involved, the above explanation would not be valid. However, this coplanar ion should not intervene in this process because it is estimated by molecular orbital calculations[18] to be 19–22 kcal/mol less stable than the normal perpendicular ion.

In the acetolysis of the primary tosylates **7** and **8**, no significant effects of cyclophanyl strain on the rearrangement were detected. The primary phenonium ions generated have a strong tendency to secondary carbenium

(16) [3.3]Paracyclophane and [6.6]paracyclophane are reported to have 12 kcal/mol and 2 kcal/mol of strain energy, respectively; as a review see ref 10.

(17) All products were stable enough under the conditions employed. Compounds **15** and **16** were not isomerized under the conditions employed here, so that S_N2 reaction of these products can be neglected.

(18) Collins, J. B.; Dill, J. D.; Jemmis, E. D.; Apeloig, Y.; Schleyer, P. v. R.; Seeger, R.; Pople, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5419–5427, and references cited therein.

Table II. First-Order Rate Constants for Acetolysis of Tosylates in 0.05 M NaOAc-Buffered Acetic Acid and Activation Parameters

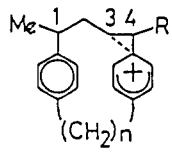
tosylate	para-cyclophane skeleton	temp, °C	$10^6 k_t$, s^{-1}	k_{rel} at 40 °C	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	temp range, °C
7a	[3.3]	70.03 ± 0.13	1050 ± 4		23.4	-4.10	50–70
7b	[3.4]	70.11 ± 0.13	369 ● 1		24.5	-2.79	50–70
7c	[3.5]	70.05 ± 0.17	266 ± 2		21.8	-11.6	60–80
8c	[3.5]	70.01 ± 0.18	202 ± 1				
7d	[3.6]	70.05 ± 0.14	165 ± 1		22.9	-9.65	60–80
8d	[3.6]	70.04 ± 0.12	114 ● 1				
22a	[4.3]	60.02 ± 0.08	1780 ± 10		20.1	-10.9	40–60
22d	[4.6]	59.97 ± 0.13	68.4 ± 1.0		22.4	-10.3	60–80
12[a]		50	1.34[b]				
10a	[3.3]	40.01 ± 0.09	1330 ● 40	152	20.2	-7.26	23–40
10b	[3.4]	39.98 ± 0.12	362 ± 8	41	21.0	-7.34	30–50
10c	[3.5]	40.03 ± 0.13	228 ± 3	26	20.4	-10.0	30–50
10d	[3.6]	40.07 ± 0.15	78.0 ± 0.8	8.9	22.3	-5.97	40–60
11		40.02 ± 0.08	13.8 ± 0.3	1.6	24.0	-4.21	40–60
13		40.01 ± 0.09	8.76 ± 0.21	1.0	23.2	-7.80	40–60

[a] See ref 2. [b] For Fk_{Δ}.

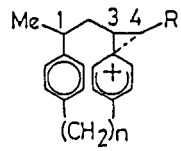
ions.[19] Therefore, we changed the substrate to secondary tosylates, which should generate cations with less tendency to rearrange than the primary analogues.

The secondary tosylates **10**, which were ~4:1 mixtures of threo and erythro isomers, gave olefins **25**, rearranged acetates **26**, and unrearranged acetates **27**. Product distributions are summarized in Table I. All products **25**, **26**, and **27** were also ~4:1 mixtures of isomers, indicating that there was no significant inversion at the solvolysis center. Accordingly, the solvolysis proceeded primarily via the phenonium ion. Since the cyclophanyl group can be regarded as more electron donating than a *p*-tolyl group, these results are reasonable; i.e., *threo*-3-(*p*-tolyl)-2-butyl brosylate was solvolyzed to its acetate via the phenonium ion in 88% yield with 100% retention of configuration.[2] Actolyses of the secondary tosylates **10** gave clear evidence of the strain effect. Thus the most strained [3.3]paracyclophane afforded mainly rearranged ring-opened acetate **26a**, the least strained [3.6]paracyclophane gave unrearranged acetate **27d** exclusively, and the intermediately strained [3.4]- and [3.5]paracyclophanes produced mixtures of **26** and **27** (see Scheme IV).

These results show the involvement of two different kinds of phenonium ions **29** and **30** in the solvolysis of tosylates **7** and **10**. Although both are unsymmetrically bound to two aliphatic carbons, ion **29** has a tighter bond to carbon 4 than to carbon 3, and ion **30** is more tightly bound to carbon 3 than to carbon 4. Consequently, the structure of the phenonium ion is changed by both the stability of the carbenium ion and the strain of the cyclophanyl system.



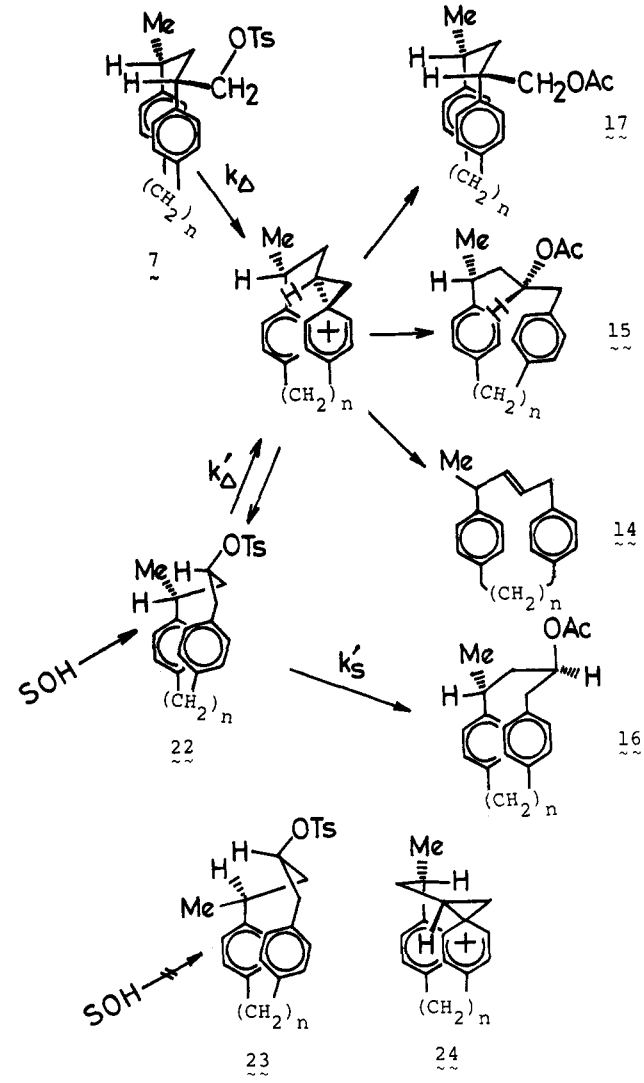
29



30

3. Rate of Acetolysis. The solvolyses were followed up to 80–90% consumption of the tosylates by analyzing the solvolysis mixtures for tosylates by reversed-phase HPLC at 30 °C, using a Develosil-PYE-packed column[20] and MeOH–H_2O (100:0 to 80:20) as eluent. The representative rate constants k_t and thermodynamic parameters are summarized in Table II. .

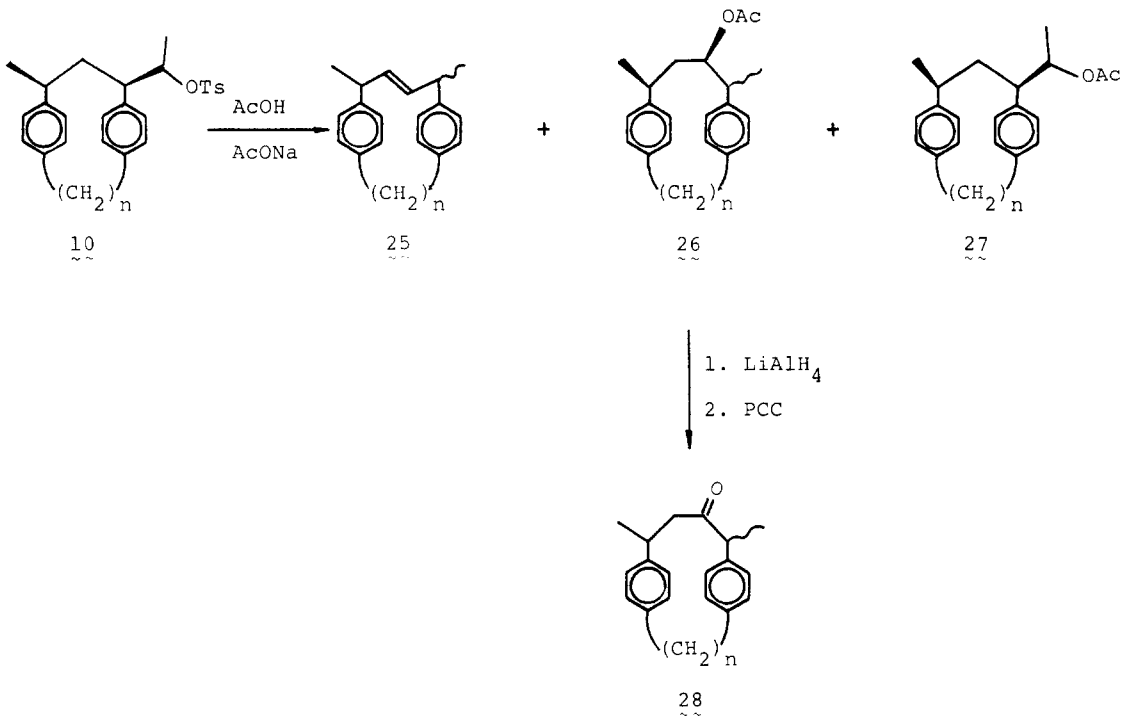
Scheme III



The large rate enhancement of solvolysis by the cyclophanyl groups is shown by comparison of the rates of **7**, **8**, and **10** with those of reference compounds **11** and **13**. The acetolysis rate k_t of **7** is the sum of the rates of **7** and **22** involved in the system.[21] The acetolysis, however, gave

(19) Radon, L.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1972**, *94*, 5935–5945.
(20) Tanaka, N.; Tokuda, Y.; Iwaguchi, K.; Araki, M. *J. Chromatogr.* **1982**, *239*, 761–772.

Scheme IV



steady first-order rate constants from the beginning and only one tosylate peak was observed throughout the experiment. According to Winstein's kinetic treatment,[21] $k_r/(k_{ts} - k_r - k_{tp})$ should be nearly equal to the initial **22**/**7** substrate ratio, which was zero in our experiments. Otherwise, we would not have observed the steady first-order kinetic behavior in this solvolysis. And k_t observed in this work is equal to $(k_r + k_{tp})$.[22] We have not been able to partition k_t among the individual rate constants, and further work will be necessary to determine the magnitude of the cyclophanyl group effect on the primary tosylates.

On the other hand, the overall rate constant of 3-(tosyloxy)[4.*n*]paracyclophane **22** can be easily divided into k_s' and Fk_Δ' by using the isomer ratios of **14**, **15**, and **16**.[21] The Fk_Δ' value of **22a** is 618×10^{-6} s^{-1} at 50 °C, while the value for **12** is reported to be 1.34×10^{-6} s^{-1} at 50 °C.[2] Hence the rate enhancement caused by the [3.4]paracyclophanyl group in the intraannular secondary tosylate is several hundred times larger than that of one aromatic nucleus, assuming that the F value of **22a** is not much different from that of **12**.

Tosylate **10a** is solvolyzed much faster than **22a**, which can be considered a model of the rearranged tosylate. Also, **10d** gave a small amount of rearranged products, although its relatively slow acetolysis might be influenced significantly by a rearrangement if one occurred. Therefore, we conclude that the rearrangement of tosylates **10** via internal return is not so significantly involved in the acetolysis. Hence the overall acetolysis rate constant k_t of **10** can be directly compared with the rate constant of **13** to determine the rate enhancement caused by the cyclophanyl groups. The rate ratios of **10** and **13** are listed in Table II. Note that the ratio of **10a** and **13** is 152. It is interesting to compare the value with those of related systems. As mentioned earlier, the [2.2]paracyclophanyl group shows only a little enhancement.[11] The enhancement caused by the *p*-methoxy group in the acetolysis of β-phenethyl tosylate (a primary tosylate) is reported to be 32 ($= k_t^{p\text{-MeO}}/k_t^{p\text{-H}}$),[2] also considerably smaller than that of **10a**, even though **10a** is a less electron-demanding secondary tosylate.

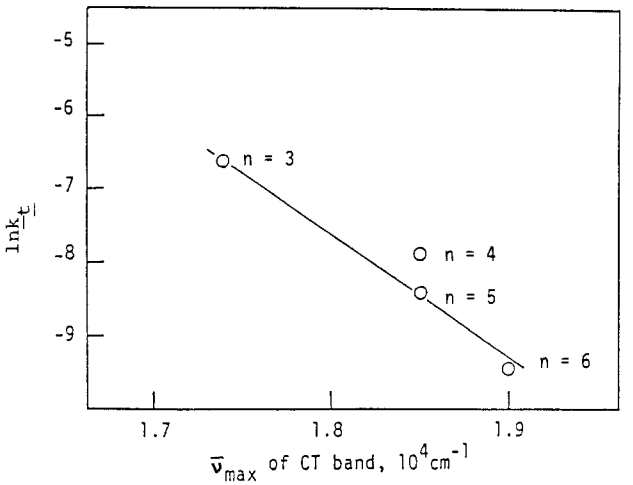


Figure 1. Acetolysis of secondary tosylates and $\bar{\nu}_{max}$ for CT band of cyclophane–TCNE complex.

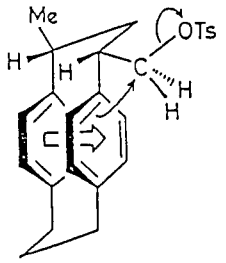
Figure 1 shows the correlation between the values of ln k_t for the secondary tosylates and $\bar{\nu}_{max}$ of the charge transfer (CT) band of the *cis*-1-methyl-3-styryl[3.*n*]paracyclophane–tetracyanoethylene (TCNE) complex.[13] The $\bar{\nu}_{max}$ of the CT band is considered to be a measure of the π-overlapping effect[9] because the $\bar{\nu}_{max}$ value depends on the electron-donating nature of the cyclophane. The coefficient of correlation is 0.935.[23] Therefore, the rate enhancement observed in the acetolyses of [3.*n*]para-

(21) (a) Winstein, S.; Schreiber, K. C. *J. Am. Chem. Soc.* **1952**, *74*, 2171–2178. (b) Diaz, A. F.; Winstein, S. *J. Am. Chem. Soc.* **1969**, *91*, 4300–4302.

(22) See eq 13 and 18 in ref 21a.

(23) The value for [3.4]paracyclophane system did not fit the correlation well. Without the point, the coefficient of correlation becomes 0.9946. The tetramethylene linkage is known not to be good for the face-to-face arrangement of 1,4-substituents because the linkage must have one eclipsed C–C bond. In the solvolysis transition state, the rather strong electron demand causes the cyclophane to attain better overlapping between the two benzene rings, but in the TCNE complex, the electron demand is too weak to force it to deform. This is considered to be the reason for the deviation.

cyclophanylmethyl tosylates is due to the anchimeric assistance of the electron-donating [3.n]paracyclophanyl group. Although the geometrical reason suggested by Hedaya and Kyle may be partly responsible,[11] the remarkable difference in the rate enhancement of the [2.2]- and [3.3]paracyclophane systems is mainly ascribed to the difference in their electron-donating nature. This difference can be indicated by the λ_{max} of CT band of their TCNE complexes as follows:[9a] [2.2]paracyclophane, 521 nm; [2.3]paracyclophane, 511 nm; [3.3]paracyclophane, 599 nm; [3.6]paracyclophane, 520 nm.



Experimental Section

Methods. NMR spectra were recorded on a Varian XL-200 NMR spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. IR spectra were taken on a JASCO IRA-1 spectrometer. Mass spectra were recorded on a Hitachi M80A mass spectrometer. GC analysis was done by a Shimadzu GC-4CIT gas chromatograph (SE-30 30%, 3 m, 250–300 °C). HPLC was carried out by using an Altex Model 110A pump, a Hitachi 635 T wavelength tunable effluent monitor, and a Knauer 98.00 differential refractometer. Melting points were not corrected.

Materials. Commercially available highest grade reagents and solvents were used without further purification. Olefins St-Cn-St were prepared conveniently by our method.[24]

The cationic cyclocodimerization was carried out by the method reported.[13] Yields are listed in Scheme I. Compounds **1a**,[13] **2a**,[13] and **1b** (mp 31.2–33.5 °C) are crystalline, but others are oils.

***cis*-1-Formyl-3-methyl[3.3]paracyclophane (3a; General Procedure).** Cyclophane **1a** (2.0 g) was ozonized with a slight excess of ozone in CCl_4 (200 mL) at 0 °C. After evaporation of the solvent, the reaction mixture was diluted with ether and added dropwise into an ethereal suspension of $LiAlH_4$ (3.0 g/50 mL). After workup, the condensed mixture was oxidized by PCC (3.1 g) in CH_2Cl_2 (300 mL). The products were purified by column chromatography (SiO_2, benzene). Yields were listed in Scheme I.

***cis*-1-Methyl-3-(hydroxymethyl)[3.3]paracyclophane (5a; General Procedure).** An ethereal solution of aldehyde **3a** (329 mg/50 mL) was added to a suspension of $LiAlH_4$ in ether (500 mg/50 mL). Alcohol **5a** was isolated after the ordinary workup and purified by column chromatography (SiO_2, benzene). Yields were quantitative. Melting points (°C) are as follows: **5a**, 131.0–134.0; **5b**, 156.1–157.1; **5c**, 144.4–147.0; **5d**, 111.8–112.7; **6a**, 119.2–123.4; **6b**, 152.5–155.0; **6c**, 116.0–117.0; **6d**, 63.0–64.0; **19a**,[25] 100.2–102.0; **19d**,[25] oil.

***cis*-1-(1-Hydroxyethyl)-3-methyl[3.3]paracyclophane (9a; General Procedure).** An ethereal solution of aldehyde **3a** (1.3 g/100 mL) was added to an ether solution of MeMgI (prepared from 2.0 g of Mg and 12.0 g of methyl iodide). Alcohol **9a** was obtained after the usual workup and purified by column chromatography (SiO_2, benzene). Yields were listed in Scheme I. Melting points (°C) are as follows: **9a**, 105.1–107.0; **9b**, 122.8–124.5; **9c**, 103.2–104.8; **9d**, 66.5–69.2.

***cis*-1-Methyl-3-((tosyloxy)methyl)[3.3]paracyclophane (7a; General Procedure).** Alcohol **5a** (12.8 mg) was added to a cold pyridine solution of *p*-toluenesulfonyl chloride (20 mg/0.4 mL). The mixture was allowed to stand at 0 to 25 °C. After the starting alcohol disappeared (TLC monitor), the solution was poured into cold water and extracted with ether. The combined extract was washed with cold water and cold dilute HCl, dried over anhydrous Na_2SO_4, and condensed by evaporation at low temperature. The purity of the tosylate (>95%) was analyzed by the 200-MHz ^1H NMR spectrometer.

Solvolysis. Tosylate (ca. 1 mM) was dissolved in the 0.05 M NaOAc–buffered acetic acid and heated under reflux for 1 day. The reaction mixture was poured into water and extracted with benzene. The combined benzene layer was washed with water and with dilute NaOH, dried over anhydrous Na_2SO_4, and condensed by evaporation. The product components were separated by column chromatography (SiO_2, benzene–cyclohexane 1:1), and each fraction was analyzed by GC to calculate yields.

Products **17**, **18**, and **27** were assigned as the corresponding alcohols **5**, **6**, and **9**, after the treatment by $LiAlH_4$. The analyses of rearranged acetates **15**, **16**, and **26** were done after the deacetylation by $LiAlH_4$ followed by the PCC oxidation to the corresponding ketones **21** and **28**. All products gave consistent ^1H NMR spectra. Melting points (°C) are as follows: **14a**, 57.8–59.0; **14b**, 61.8–62.9; **14c**, 72.9–73.6; **14d**, 84.8–85.4; **21a**, 97.8–99.1; **21b**, 82.8–85.1; **21c**, 127.2–129.4; **21d**, 120.7–121.4; **25a**, 88.9–91.4; **25b**, 55.0–57.2; **25c**, 110.8–111.7; **25d**, 55.1–57.2; **28a**, 84.2–84.9; **28b**, 95.5–96.7; **28c**, 130.0–131.1.

Kinetic Method. Rates of the acetolysis were followed by the consumption of the tosylate. The concentration of the tosylate was measured by HPLC (Develosil PYE,[20] 30 °C, MeOH–H_2O, UV monitor at 275 nm). The procedure is as follows: The tosylate (ca. 10 mM) was dissolved in 0.05 M NaOAc–buffered acetic acid at room temperature under a nitrogen atmosphere in a test tube. The tube was immersed in the temperature-controlled oil bath and the mixture was stirred. After ca. 10 min, the first aliquot (ca. 1 mL) for the time zero was withdrawn from the mixture through a serum cap with a tight hypodermic syringe and a needle under a nitrogen atmosphere. The aliquots (at least 5 times) withdrawn from the reaction mixture at the prescribed periods were injected directly to the HPLC sample injector (20 μL). The peak area was obtained as the weight of the paper cut as the peak shape (the error within 1%). First-order rate constants were obtained from semilogarithmic plots of a_0/a against time (a = peak area of the trace of HPLC due to the substrate), which has a good linear relationship up to 80% conversion.

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Registry No. **1a**, 85781-50-6; **1b**, 101472-21-3; **1c**, 101472-22-4; **1d**, 101472-23-5; **3a**, 101472-24-6; **3b**, 101472-25-7; **3c**, 101472-26-8; **3d**, 101472-27-9; **5a**, 101472-28-0; **5b**, 101472-29-1; **5c**, 101472-30-4; **5d**, 101472-31-5; **6a**, 101540-89-0; **6b**, 101540-90-3; **6c**, 101540-91-4; **6d**, 101540-92-5; **7a**, 101472-36-0; **7b**, 101472-37-1; **7c**, 101472-38-2; **7d**, 101472-39-3; **8a**, 101540-93-6; **8b**, 101540-94-7; **8c**, 101540-95-8; **8d**, 101540-96-9; **9a**, 101472-32-6; **9b**, 101472-33-7; **9c**, 101472-34-8; **9d**, 101472-35-9; **10a**, 101472-40-6; **10b**, 101472-41-7; **10c**, 101472-42-8; **10d**, 101472-43-9; **11**, 101472-46-2; **13**, 101472-47-3; **14a**, 101472-48-4; **14b**, 101472-49-5; **14c**, 101472-50-8; **14d**, 101472-51-9; **15a**, 101472-56-4; **15b**, 101472-57-5; **15c**, 101472-58-6; **15d**, 101472-59-7; **16a**, 101540-97-0; **16b**, 101540-98-1; **16c**, 101540-99-2; **16d**, 101541-00-8; **17b**, 101472-63-3; **17c**, 101472-64-4; **18b**, 101627-07-0; **18c**, 101541-01-9; **22a**, 101472-44-0; **22d**, 101472-45-1; **25a**, 101472-52-0; **25b**, 101472-53-1; **25c**, 101472-54-2; **25d**, 101472-55-3; **26a**, 101472-60-0; **26b**, 101472-61-1; **26c**, 101472-62-2; **27b**, 101472-65-5; **27c**, 101472-66-6; **27d**, 101472-67-7.

Supplementary Material Available: Three tables of kinetic data, one table of physical and analytical data, and ^1H NMR spectroscopic data of compounds produced (15 pages). Ordering information can be found on any current masthead page.

(24) Nishimura, J.; Ishida, Y.; Hashimoto, K.; Shimizu, Y.; Oku, A.; Yamashita, S. *Polym. J.* **1981**, *13*, 635–639.

(25) Prepared from **15** by $LiAlH_4$ reduction.