2.[14] The thermal opening of the *cis*-fused three-membered ring in compounds of type **2** has been predicted[15] to give mono-*trans*-heteronins of type **3**.

1-Phenylphosphonin oxide (**3**) was then directly observed by low-temperature (−20 °C) ^{31}P NMR spectroscopy. A peak with $\delta(^{31}P)$ +16.2 was observed, which agrees well with the value of +17.2 found for 1-phenyldibenzo[*d,f*]phosphonin 1-oxide, the only other known oxide of a phosphonin.[16] Phosphonin oxide **3** has good stability at −17 °C, but at 24 °C it decays with a half-life of about 5 min with the formation of the [4 + 2] product **4**. This half-life is much shorter than that of *cis*[4]-cyclononatetraene[16] ($t_{1/2}$ 50 min at 23 °C). The ^{13}C NMR spectrum was also taken on the reaction product while still at −20 °C but was too complex for full analysis. Confirming points for structure **3**, however, were the presence of downfield signals ($\delta \sim 154$) typical of sp^2 carbons β to P=O and the absence of sp^3 carbons.

Oxidation of **1** by oxygen follows a different pathway and does not lead to **3**.

This technique is being used in the synthesis of other phosphonin oxides and may constitute a route to the still-unknown thionin oxide system.

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(15) Anastassiou, A. G. *J. Am. Chem. Soc.* **1968**, *90*, 1527.
(16) Quin, L. D.; Middlemas, E. D.; Rao, N. S. *J. Org. Chem.* **1982**, *47*, 905.

Doubly Destabilized Carbocations. Unexpectedly High Reactivity in Formation of Carbocation Intermediates with Two Destabilizing Substituents

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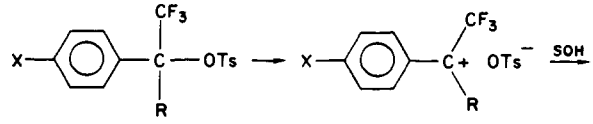
Carbocations bearing groups such as CF_3[1] and CN[2] may be termed electron deficient[3a] relative to hydrogen-substituted analogues and are destabilized[3b] in comparison to these species. Efforts to study carbocations substituted with two such groups have been inconclusive. Thus attempts to form long-lived carbocations bearing two α-CF_3 groups were not successful,[4] and although Astrologes and Martin[5] presented convincing evidence that the triflate corresponding to **1a** underwent methanolysis via a carbocation, the absence of suitable comparative data precluded a quantitative estimate of the rate deceleration.

We have now studied the reactivities of **1a–d**, which give the solvolytic rate constants reported in Table I, and which proceed with substitution by the solvent to give **2** as major products. The dependence of the rates of **1b** on the solvent polarity parameter Y_{OTs}[6] is $\log k = 0.76Y_{OTs} - 3.30$, and the rates of **1a–c** in CF_3CO_2H at 25 °C gave the relation $\log k = -10.7\sigma^+ - 8.65$. All these results support the mechanism of eq 1 with intervention of carbocation intermediates bearing two electron-withdrawing groups.

Table I. Solvolysis Rates of ROTs (1)[a]

ROTs	T, °C	solvent[c]	k_1, s^{-1}	ΔH^*, kcal/mol	ΔS^*, eu
1a	121.0	TFA	2.53×10^{-5}		
	111.5		1.20×10^{-5}		
	96.5		3.56×10^{-6}		
	25.0[b]		1.94×10^{-9}	22.4	−23.4
1b	25.0[b]	TFA	0.470	20.7	9.5
	19.1		0.235		
	12.7		9.50×10^{-2}		
	4.0		3.15×10^{-2}		
1b	25.0	TFE	2.10×10^{-2}	16.8	−9.9
	12.7		5.81×10^{-3}		
	4.0		2.28×10^{-3}		
1b	56.4	HOAc	3.55×10^{-4}		
	41.2		6.46×10^{-5}		
	25.0		8.00×10^{-6}	23.0	−4.8
1b	25.0	HFIP	0.235		
	25.0	HCO_2H	2.02×10^{-2}		
	25.0	80% EtOH	2.52×10^{-4}		
	25.0	100% EtOH	3.00×10^{-5}		
1c	121.0	TFA	1.06×10^{-4}		
	105.9		3.98×10^{-5}		
	91.4		1.12×10^{-5}		
	25.0[b]		1.53×10^{-8}	20.9	−24.1
1d	115.0	TFA	7.66×10^{-4}		
	100.9		2.73×10^{-4}		
	80.5		4.18×10^{-5}		
	25.0[b]		9.69×10^{-8}	22.4	−15.6

[a] Duplicate runs at each temperature, ±5%. [b] Extrapolated from data at other temperatures. [c] TFA is CF_3CO_2H, TFE is 97% CF_3CH_2OH, HFIP is 97% $(CF_3)_2CHOH$.



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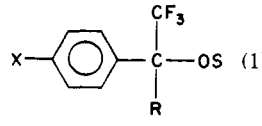

(1)

2

a, R = CF_3; X = H
b, R = CF_3; X = MeO
c, R = CF_3; X = F
d, R = CN; X = H
e, R = CH_3; X = H
f, R = H; X = H

The rate of **1f**[1a] relative to **1a** is 54 at 25 °C in CF_3CO_2H. Corresponding $k(H)/k(CF_3)$ ratios for **1b** are 2.4–5.2 (six different solvents) and for **1d** the ratio is 1.1. These ratios are extraordinarily small: values for substrates with only one destabilizing group range from 2×10^3 to 10^7 for CF_3[1] and 10^2 to 10^6 for CN.[2]

Three of the possible causes for the unexpectedly high reactivity of **1a–d** include strong electron donation by the group R, ground-state strain, and charge delocalization onto the aryl group. As to the first of these, π-electron donation by CN is well documented,[2] but for CF_3 theoretical studies[7] suggest this effect will be considerably less important.

(1) (a) Allen, A. D.; Ambidge, I. C.; Che, C.; Michael, H.; Muir, R. J.; Tidwell, T. T. *J. Am. Chem. Soc.* **1983**, *105*, 2343–2350. (b) Allen, A. D.; Jansen, M. P.; Koshy, K. M.; Mangru, N. N.; Tidwell, T. T. *Ibid.* **1982**, *104*, 207–211 and references therein.
(2) (a) Gassman, P. G.; Guggenheim, T. L. *J. Org. Chem.* **1982**, *47*, 3023–3026. (b) Gassman, P. G.; Doherty, M. M. *J. Am. Chem. Soc.* **1982**, *104*, 3742–3744 and references therein.
(3) (a) Gassman, P. G.; Tidwell, T. T. *Acc. Chem. Res.*, in press. (b) Tidwell, T. T. *Angew. Chem.*, in press.
(4) Olah, G. A.; Pittman, C. U., Jr. *J. Am. Chem. Soc.* **1966**, *88*, 3310–3312.
(5) Astrologes, G. W.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 4400–4404.
(6) (a) Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7658–7666. (b) Bentley, T. W.; Bowen, C. T.; Morten, D. H.; Schleyer, P. v. R. *Ibid.* **1981**, *103*, 5466–5475.
(7) (a) Paddon-Row, M. N.; Santiago, C.; Houk, K. *J. Am. Chem. Soc.* **1980**, *102*, 6561–6563. (b) Reynolds, W. F.; Dais, P.; MacIntyre, D. W.; Topsom, R. D.; Marriott, S.; Nagy-Felsobuki, E. V.; Taft, R. W. *Ibid.* **1983**, *105*, 378–384.

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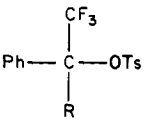
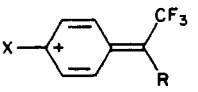
Table II. Bond Angles in 1-Phenyl-2,2,2-trifluoroethyl Tosylates



compd	R	PhCOTs	$PhCCF_3$	PhCR	CF_3CR	CF_3COTs	RCOTs
1e	CH_3	110	110	114	109	100	113
1a	CF_3	115	109	115	107	102	108
1d	CN	114	111	112	107	102	110

Ground-state strain is a possible contributor to the reactivity of the highly substituted substrates **1**, and indeed X-ray crystal structure analyses[8] of **1a**, **1d**, and **1e** reveal each to be distorted from the tetrahedral, as illustrated by the bond angles at the central carbon (Table II). The differences between the largest and smallest angles range from 12° to 14° for the different substrates, comparable to those in tri-*tert*-butylcarbinyl *p*-nitrobenzoate,[9] a compound for which ground-state strain is generally accepted as a major contributor to the observed reactivity. As **1a**, **1d** and **1e** are all distorted there is no sure basis to ascribe the anomalously high reactivity of **1a** and **1d** relative to **1f** to ground-state strain, particularly as the quantitative relationship between geometries and energetics is not known. Bond lengths C–OTs for **1a**, **1d**, and **1e** are 1.436, 1.432, and 1.457 Å, respectively, while relative reactivities in TFA at 25 °C are 1.0, 50, and 2.6×10^7, respectively. The significantly greater reactivity and bond length of **1e** are consistent with a proposed[10] correlation between these properties.

A plausible explanation consistent with all the results is that the transition states for reaction of **1a-c** and **1f** all resemble **3** with



3

the charge delocalized onto the aryl ring. Consequently the difference in the effect of R (H or CF_3) is small. The fact that ρ^+ values when R = H[1a] and CF_3 are similar supports this interpretation. When R = CH_3 or when the CF_3 group is not present there is less electron demand and a lower effect of X.

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Registry No. 1a, 86669-60-5; **1b**, 86688-54-2; **1c**, 86669-61-6; **1d**, 86669-62-7; **1e**, 73572-26-6; **1f**, 13652-13-6.

(8) We thank Dr. J. F. Sawyer for these determinations, details of which will be reported elsewhere.

(9) Cheng, P.-T.; Nyburg, S. C.; Thankachan, C.; Tidwell, T. T. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 654–655.

(10) Jones, P. G.; Kirby, A. J. *J. Chem. Soc., Chem. Commun.* **1979**, 288–289.

*Book Reviews**

Topics in Current Chemistry. Volumes 98 and 101. Host Guest Complex Chemistry I and II. Edited by F. Vögtle. Springer-Verlag, Berlin, Heidelberg, and New York. Volume 98: 1981. 197 pp. $35.00. Volume 101: 1982. 203 pp. $37.50.

These two volumes consist of reviews covering fundamental aspects and applications of complexes formed between cavity-containing ligands, hosts, and small neutral molecules or ions, guests. Volume 98 contains four chapters, focusing on the structure, complexation properties, and analytical applications of a wide variety of host compounds. The first chapter of Volume 98, Crown-Type Compounds—An Introductory Overview (E. Weber and F. Vögtle), provides a short survey of the field. The main topics covered include classification and nomenclature of macrocyclic and acyclic ligands, general complexation properties of crown-type compounds, and effects of complexation on the chemical properties of the guest particles. The relationship between the structure and complexation properties of crown-type hosts is treated in detail in the section titled Concept, Structure, and Binding in Complexation (D. Cram and K. Trueblood). This chapter is not a general survey but deals primarily with work from the authors' laboratory, with emphasis on macrocycles containing rigid structural units, the spherands, and hemispherands. The use of molecular models and X-ray structural analysis in the design of host molecules, structural changes accompanying host complexation, and correlation of the structure with free energy of complexation are the main topics in this section. The third chapter, Complexation of Uncharged Molecules and Anions by Crown-type Host Molecules (F. Vögtle, H. Sieger, and S. W. Möller), surveys in detail the work done on inclusion complexes of small molecules with coronand, cryptand, and catapinand type ligands. Complexes of acyclic neutral ligand hosts with small guest molecules are also treated. Minor topics include complexes with hosts containing lipophilic cavities, complexes with anions as guests, and multicomponent complexes. Volume 98 concludes with a short chapter titled Analytical Applications of Crown Compounds and Cryptands (E. Blasius and K.-P. Janzen). This chapter focuses primarily on the applications of monomeric and polymeric cyclic polyethers in chemical separation. Extraction and chromatographic methods are the primary subject areas. Brief accounts are given of the uses of cyclic polyethers in photometric and electrochemical determination methods.

The topics covered in Volume 101 cover a broad range of subjects in the field of host–guest chemistry. The first article, Structural Chemistry of Natural and Synthetic Inophores and Their Complexes with Cations (R. Hilgenfeld and W. Saenger), is a selective review of the crystal structures of a wide variety of ionophores and their metal ion complexes. Included in the review are the naturally occurring peptide and polyether antibiotics, synthetic macrocyclic and macrobicyclic ligands, and the open-chain polyethers or podands. Comparisons between the ligand conformation(s) in the free and complexed form in the solid state are made, and, whenever possible, solution and solid-state structural data are compared. Comprehensive compilations of published crystal structures are included for each type of ionophore.

A second chapter on ionophores, Dynamic Aspects of Ionophore Mediated Membrane Transport (G. Painter and B. Pressman), deals primarily with membrane transport processes of naturally occurring polyether carboxylic acid ionophores. The conformational dynamics of selected ionophores in bulk solvents of varying polarity are related to the conformational dynamics of these ionophores during the cation transport process and the effects of specific ionophore–membrane interactions are discussed. A short treatment of the biological properties of ionophores, with emphasis on cardiovascular effects and monovalent cation transport across red blood cell membranes, concludes this chapter. The third section of this volume is Bioorganic Modelling-Stereoselective Reactions with Chiral Neutral Ligand Complexes as Model Systems for Enzyme Catalysis (R. Kellogg). This chapter reviews the application of macrocyclic compounds as model systems for certain enzymatic processes. The

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