Table II. Partitioning of Rate Constants for β-Arylethyl Tosylates at 115°

		Substrate: X =			
		p-Cl	H	p-CH$_3$	p-CH$_3$O
$k_s \times 10^7$, sec^{-1}	This work[a]	70	73	76	78
	Coke, Jones[b]	64 ± 0.1[d]	79 ± 11	78 ± 44	282[e] ± 250
$Fk_\Delta \times 10^7$, sec^{-1}	This work[a]	15	54	354	3922
	Coke, Jones[b]	6.1 ± 0.08	48 ± 11	352 ± 43	4807[e] ± 419
$\Delta S^{\ddagger}$ (k_s), eu	This work[a]	−22	−22	−22	−22
	Coke, Jones[b]	−25 ± 1	−21 ± 2	−24 ± 8	
$\Delta S^{\ddagger}$(Fk_Δ), eu	This work[a]	−8	−15	−12	−10
	Coke, Jones[b]	−26 ± 8	−12 ± 1	−12 ± 1	−9 ± 1
(Fk_Δ/k_t) × 100	This work[a]	18	42	82	98
	Coke, Jones[b]	8.7 ± 0.1	38 ± 8.5; 32[c]	82 ± 10	95
k_t/k_s This work[a]		1.21	1.73	5.63	51.1

[a] Hammett treatment. [b] ^{14}C scrambling combined with kinetic data.[5] [c] Per cent retention of configuration in *threo*-1,2-dideuterio derivative.[10] [d] Since Coke and Jones's[5] treatment consists of two data sets with somewhat differing results, we have followed their approach of listing the average value together with the error spread from either data set. Our treatment consists of a single data set in which the intrinsic error in the successive approximations[8] is difficult to assess quantitatively. An estimate of ±7% can be made from the scatter in the Fk_Δ *vs.* σ^+ plot. [e] Calculated from data at other temperatures.

Table II compares the values for k_s, Fk_Δ, $\Delta S^{\ddagger}(k_s)$, and $\Delta S^{\ddagger}(Fk_\Delta)$ estimated in the present study with those derived from Coke and Jones's combination of ^{14}C scrambling and kinetic data.[5] Rate and product data also may be conveniently compared *via* the percentage of aryl participation, $(Fk_\Delta/k_t) \times 100$. These values are included in Table II. For all substrates, the agreement between the two methods is remarkably good. In addition, good agreement is obtained with the purely product-derived result of Snyder and Jablonski for *threo*-1,2-dideuterio-2-arylethyl tosylate.[10]

The close agreement between rate and product data provides the first direct experimental evidence that the assumption[4,5] of discreteness between the solvent-assisted (k_s) and aryl-assisted (Fk_Δ) pathways is valid for such primary systems. The solvent-assisted reaction is essentially an SN2 process; the magnitude of ρ_s (−0.10 at 115°) is very low,[12,13] indicating that virtually no positive charge is generated on carbon in the transition state. $\Delta S^{\ddagger}(k_s)$ is remarkably constant, −22 eu, and about 10 eu more negative than $\Delta S^{\ddagger}$ (Fk_Δ).[14] This difference is almost certainly due to ordering of the solvent in the SN2-like transition state.[15]

In the aryl-assisted pathway (Fk_Δ), the high degree of charge delocalization into the participating aryl nucleus is revealed by the value of ρ^+, −2.4 at 115°.[16,17] Although the rate enhancements, as measured by k_t/k_s (Table II), are often of relatively small magnitude, this should not be taken to indicate that bridging is weak in the transition state.[18] Rather, as we have noted previously,[1] aryl assistance, in order to be seen at all, must be greater than the already efficient solvent assistance against which it is competing.

Acknowledgments. We thank the National Science Foundation, the Petroleum Research Fund, administered by the American Chemical Society, and the National Institutes of Health (AI-07766) for support of this research. We thank Mr. Paul Garrison of the FMC Corporation for the figure.

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(12) Typical ρ_s values for secondary and tertiary aryl-unassisted processes are −0.7[1a] and −1.0,[13] respectively.

(13) H. C. Brown and C. J. Kim, *J. Am. Chem. Soc.*, 90, 2082 (1968); M. Tessler and C. A. VanderWerf, *J. Org. Chem.* 30, 405 (1965).

(14) S. Winstein and R. Heck, *J. Am. Chem. Soc.*, 78, 4801 (1956); D. J. Cram and L. A. Singer, *ibid.*, 85, 1075 (1963).

(15) See ref 5 for a summary of pertinent references.

(16) *Cf.* ρ^+ (Fk_Δ) = −2.96 for the neophyl system at 75° (R. Heck and S. Winstein, *J. Am. Chem. Soc.*, 79, 3432 (1957)).

(17) Since F is nearly constant for all participating substrates,[5] plots of either log k_Δ or of log Fk_Δ *vs.* σ^+ will give essentially the same ρ^+ value.

(18) H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, *J. Am. Chem. Soc.*, 89, 370 (1967).

(19) National Institutes of Health Postdoctoral Fellow, 1969–1970.

(20) National Institutes of Health Predoctoral Fellow, 1969–1970.

(21) American Can Company Fellow, 1966–1967; National Institutes of Health Predoctoral Fellow, 1967–1968; Ph.D. Thesis, Princeton University, 1969.

J. Milton Harris,[19] Frank L. Schadt[20]
Paul von R. Schleyer
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

Charles J. Lancelot[21]
Chemical Research and Development Center
FMC Corporation, Princeton, New Jersey 08540

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Ionic Reactions of Carbon Tetrachloride. Survey of Reactions with Ketones, Alcohols, and Sulfones

Sir:

We have found that CCl$_4$ reacts rapidly with ketones, alcohols, and sulfones in the presence of KOH, leading to a variety of products often in high yields. Some of the products are derived from dichlorocarbene generated in the reactions. This communication surveys the types of reactions we have investigated (Table I).[1] Kinetic, mechanistic, and experimental details will be presented in subsequent reports.

Ketones. Ketones with α but no α' hydrogens (class I) are readily poly-α-chlorinated and may subsequently be cleaved into carboxylic acids (*cf.* the haloform reaction). Ketones with α and α' hydrogens (class II) are transformed *in situ* into the carboxylic

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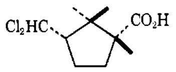
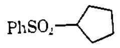
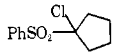
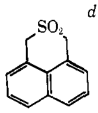
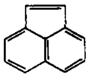
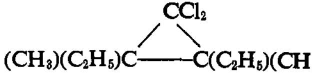
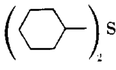
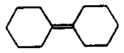
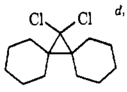
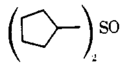
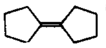
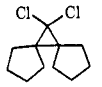
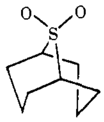
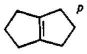
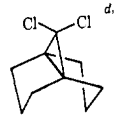
(1) General reaction conditions per gram of substrate: 3–6 g of powdered KOH, 1–10 ml of *t*-BuOH, 1 ml of H$_2$O, 10 ml of CCl$_4$, 25–80°, 10–60 min, vigorous stirring. In some cases additional H$_2$O replaced the *t*-BuOH.

Table I. Reactions of CCl_4 with Ketones, Alcohols, and Sulfones[a]

Substrate	Class[b]	Product	Yield, %[c]
	Ketones		
$(CH_3)_3CCOCH_3$	I	$(CH_3)_3CCO_2H$	80
Camphor		 ^{d,e}	70
$Ph_2CHCOCH_3$	II	$Ph_2CHCH_2CO_2H$	70
$(CH_3)_2CHCOCH_3$		$(CH_3)_3CCO_2H$	70
		$(CH_3)_3CCO_2C(CH_3)_3$[f]	20–50
$c\text{-}C_6H_{11}CH_2COCH_3$		$c\text{-}C_6H_{11}CH(CH_3)CO_2H$	60
	Alcohols		
$PhCH_2OH$	I	$PhCO_2H$	75
$o\text{-}HOC_6H_4CH_2OH$		$o\text{-}HOC_6H_4CHO$	(60) 16
$(CH_3)_3CCH_2OH$		$(CH_3)_3CCHO$	20
		$(CH_3)_3CCO_2CH_2C(CH_3)_3$	10
		$(CH_3)_3CCO_2H$	10
$Ph_2CHCH(CH_3)OH$	II	$Ph_2CHCH_2CO_2H$	(43) 25
$(CH_3)_2CHCH(CH_3)OH$		$(CH_3)_3CCO_2H$	25
Ph_2CHOH		Ph_2CO	100
	Sulfones		
$PhSO_2CH(CH_3)Ph$	I	$PhSO_2C(Cl)(CH_3)Ph^{d,g}$	100
^{d,h} 		^{d,i} 	100
$PhSO_2CH_2Ph$		$PhSO_2CCl_2Ph$	100
$PhSO_2CH_3$		$PhSO_2CCl_3$ $PhSO_3H$	100
$(PhCH_2)_2SO_2$	II	*trans*-PhCH=CHPh	100
$(Ph(CH_3)H)_2SO_2$		$Ph(CH_3)C{=}C(CH_3)Ph$	100
dl		*cis,trans*	28, 72
meso		*cis,trans*	90, 10
 ^{d,j}			45
$(CH_3CH_2C(CH_3)H)_2SO_2$	III	$(CH_3)(C_2H_5)C{=}C(C_2H_5)(CH_3)$  $(CH_3)(C_2H_5)C\overset{CCl_2}{\text{———}}C(C_2H_5)(CH_3)^{d,k}$;	90
		 ^{l}	32
		 ^{d,m}	60
		 ^{n}	(30) 15
		 ^{d,n}	(45) 25
 ^{o}		 ^{p}	(45) 30
		 ^{d,q}	(50) 35

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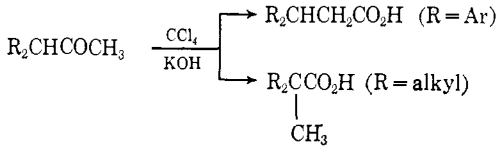
[a] General reaction conditions are given in ref 1. [b] Roman numerals refer to classifications noted in the text. [c] Yields are those actually obtained by isolation; figures in parentheses are based on unrecovered substrate. [d] Previously unreported; characterized by microanalysis (Galbraith Laboratories, Knoxville, Tenn.) and ir and nmr spectra. [e] Mp 128°; $[\alpha]^{28}D$ +43.2° (*c* 7.5, absolute EtOH). [f] From reaction carried out in anhydrous *t*-BuOK–*t*-BuOH; pivalic acid (10–20%) was also isolated. [g] Mp 134–135°. [h] Mp 60.5–61.5°. [i] Mp 112–113°. [j] Mp 238–241°; we are grateful to Professor L. A. Carpino and Dr. G. Soldati for providing us with this compound. [k] ν_{max}^{neat} 850 cm^{-1}, very intense; a very intense band near 850 cm^{-1} exhibited by 1,1-dichlorocyclopropanes was reported by W. von E. Doering and A. K. Hoffman, *J. Amer. Chem. Soc.*, **76**, 6162 (1954). [l] $\delta_{TMS}^{CDCl_3}$ 2.18 (triplet, 8 α-H), and 1.51 (multiplet, 12 β- and γ-H). [m] Mp 83.5–85°; $\delta_{TMS}^{CDCl_3}$ 1.58 (sharp singlet); $\nu_{max}^{CS_2}$ 840 cm^{-1}, very intense (*cf.* footnote *k*). [n] The combined products were removed from unchanged sulfone but not separated; vpc indicated an adduct:alkene ratio of 7:3, the adduct exhibiting the longer retention time and a band ν_{max}^{neat} 845 cm^{-1}, very intense (*cf.* footnote *k*). [o] We are grateful to Professor L. A. Paquette and Mr. R. W. Houser for providing a sample of the sulfide which we converted into the sulfone. [p] $\delta_{TMS}^{CDCl_3}$ 2.18 (sharp singlet); ir exhibited no features other than those expected from a symmetrically tetrasubstituted olefin (*cf.* ref 5c). [q] White needle clusters *via* sublimation, mp 40.5–41.5°; $\delta_{TMS}^{CDCl_3}$ 2.05 (sharp singlet); $\nu_{max}^{CS_2}$ 859 cm^{-1}, very intense (*cf.* footnote *k*).

acids expected to be formed from the corresponding α-chloro ketones *via* the Favorskii reaction (eq 1).[2]



$$R_2CHCOCH_3 \xrightarrow[KOH]{CCl_4} \begin{cases} R_2CHCH_2CO_2H \quad (R = Ar) \\ \underset{CH_3}{\underset{|}{R_2C}}CO_2H \quad (R = alkyl) \end{cases} \qquad (1)$$

Alcohols. Primary alcohols (class I) are oxidized to the corresponding aldehydes. The latter may subsequently undergo aldol condensations leading to polymers or the Cannizzaro reaction leading entirely to carboxylic acids. Aldehydes that are more resistant to strong alkali (*viz.*, salicylaldehyde, pivalaldehyde)[3] can be isolated. Secondary alcohols (class II) are oxidized to the corresponding ketones. If the latter possess α hydrogens they react further (*vide supra*); those bearing no α hydrogens can be isolated. Tertiary alcohols are essentially unreactive.

Sulfones. Aryl alkyl sulfones (class I) are quantitively α-chlorinated, di- and trichlorination proceeding at increased rates. Trichloromethyl sulfones are prone to nucleophilic cleavage under these alkaline conditions (eq 2).[4]

$$ArSO_2CH_3 \xrightarrow[KOH]{CCl_4} ArSO_2CH_2Cl \longrightarrow \longrightarrow ArSO_2CCl_3 \longrightarrow ArSO_3H \qquad (2)$$

Dibenzyl sulfones (class II) are rapidly converted *in situ* into the stilbenes expected to be formed from the corresponding α-chloro sulfones *via* the Ramberg–Bäcklund reaction (eq 3).[5] These reactions can be highly stereospecific, *dl* sulfones being converted mainly into *trans* stilbenes, and *meso* sulfones into *cis* stilbenes,[6] in accord with the geometries predicted and observed in Ramberg–Bäcklund reactions.[5d,e]

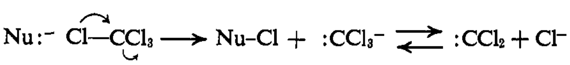
$$(Ar(R)CH)_2SO_2 \xrightarrow[KOH]{CCl_4} Ar(R)C{=}C(R)Ar \quad (R = H \text{ or alkyl}) \qquad (3)$$

Di-*sec*-alkyl sulfones (class III) are converted into alkenes as well as the alkene-dichlorocarbene adducts (1,1-dichlorocyclopropanes). The latter are often the major products, which suggests that most of the dichlorocarbene (generated in the reaction of sulfonyl carbanion with CCl_4) may react with the rapidly formed episulfone or alkene in a common transition envelope before diffusing into and reacting with the *t*-BuOH, H_2O, or KOH.[7]

Hydrocarbon anions[8] as well as *t*-BuOK[9] react with CCl_4 presumably by direct attack on chlorine, dichlorocarbene being generated. Solid KOH, even in the presence of *t*-BuOH or H_2O, reacts only slightly with CCl_4 under reflux. When appropriate ketones, alcohols, or sulfones are added a vigorous reaction occurs and an abundance of chloride ion is produced.

These observations, and the fact that the products we isolated are either the chlorinated substrates or compounds expected to be formed from them under these conditions, suggest that these reactions also involve attack by the substrate anion on chlorine of CCl_4. These chlorinations with CCl_4 are relatively slow, allowing subsequent (or concerted) reactions to occur *before* multiple chlorinations (eq 4–7). In contrast, more common halogenating agents react rapidly with anions to yield polyhalogenated species and products derived from them. The type of product ultimately formed can be significantly controlled by the difference in these relative rates,[10] *e.g.*, eq 8.

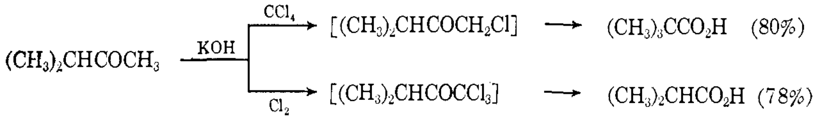
$$Nu{-}H \overset{:B^-}{\rightleftarrows} Nu{:}^- + B{-}H \qquad (4)$$



$$Nu{:}^- \; Cl{-}CCl_3 \longrightarrow Nu{-}Cl + {:}CCl_3^- \rightleftarrows {:}CCl_2 + Cl^- \qquad (5)$$

$$Nu{-}Cl \xrightarrow[(CCl_4)]{:B^-} \text{products} \qquad (6)$$

$${:}CCl_2 \xrightarrow[\text{solvent}]{\text{products}} \text{other products} \qquad (7)$$



$$(CH_3)_2CHCOCH_3 \xrightarrow{KOH} \begin{cases} \xrightarrow{CCl_4} [(CH_3)_2CHCOCH_2Cl] \longrightarrow (CH_3)_3CCO_2H \;(80\%) \\ \xrightarrow[Cl_2]{} [(CH_3)_2CHCOCCl_3] \longrightarrow (CH_3)_2CHCO_2H \;(78\%) \end{cases} \qquad (8)$$

Acknowledgment. We are grateful to the University's Office of Research and Projects for supporting this study.

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(2) Favorskii reaction mechanism studies are of current interest: (a) F. G. Bordwell and M. W. Carlson, *J. Amer. Chem. Soc.*, **91**, 3951 (1969), and preceding papers; (b) E. W. Warnhoff, C. M. Wong, and W. T. Tai, *ibid.*, **90**, 514 (1968).

(3) T. A. Geissman, *Org. Reactions*, **2**, 94 (1944).

(4) This was also observed by W. V. Ferrar, *J. Chem. Soc.*, 508 (1956).

(5) Synthetic and mechanistic aspects of the Ramberg–Bäcklund reaction have been reported recently: (a) L. A. Paquette and J. C. Philips, *J. Amer. Chem. Soc.*, **91**, 3973 (1969); (b) L. A. Paquette and R. W. Houser, *ibid.*, **91**, 3870 (1969); (c) E. J. Corey and E. Block, *J. Org. Chem.*, **34**, 1233 (1969); (d) F. G. Bordwell and E. Doomes, 157th National Meeting of the American Chemical Society, ACS, Minneapolis, Minnesota, April 1969, Abstract ORGN 55; (e) F. G. Bordwell, B. B. Jarvis, and P. W. R. Corfield, *J. Amer. Chem. Soc.*, **90**, 5298 (1968).

(6) Configurational assignment to *dl* and *meso* sulfones by means of nmr was reported by C. Y. Meyers and A. M. Malte, *ibid.*, **91**, 2123 (1969).

(7) Generally, yields of alkene–:CCl_2 adducts similar to those we observed are realized from reactions carried out with :CCl_2 generated under strictly anhydrous conditions, in the alkene as solvent; *cf.* W. E. Parham and E. E. Schweizer, *Org. Reactions*, **13**, 55 (1963).

(8) (a) W. T. Miller and C. S. U. Kim, *J. Amer. Chem. Soc.*, **81**, 5008 (1959); (b) C. R. Hauser, W. G. Kofron, W. R. Dunnavant, and W. F. Owens, *J. Org. Chem.*, **26**, 2627 (1961).

(9) (a) W. G. Kofron, F. B. Kirby, and C. R. Hauser, *ibid.*, **28**, 873 (1963); (b) C. Y. Meyers and J. A. Tykal (Midwest Regional Meeting of the American Chemical Society, Manhattan, Kans., Oct 1968, Abstracts, p 32) suggested that *t*-BuOCl is initially formed and rapidly converted into isobutylene oxide, which they isolated. This mechanism gains support by the observation of C. Walling and J. Kjellgren (*J. Org. Chem.*, **34**, 1487 (1969)) that isobutylene oxide is a major product from the exothermic reaction of *t*-BuOCl with *t*-BuOK.

(10) C. Y. Meyers and W. S. Matthews (manuscript in preparation) have also found that Favorskii and haloform reactions can be competitive when certain methyl ketones are treated with alkaline hypohalite.

(11) (a) Southern Illinois University Foundation Postdoctoral Fellow, 1968–1969; (b) University Predoctoral Fellow, 1968–1969.

Cal Y. Meyers, Ashok M. Malte,[11a]
Walter S. Matthews[11b]
Department of Chemistry, Southern Illinois University
Carbondale, Illinois 62901

Received July 28, 1969

Thermolysis of Pentacyclo[4.4.0.0.^{2,5}0.^{3,8}0^{4,7}]dec-9-ene

Sir:

Thermal conversion of pentacyclic hydrocarbon **1** to Nenitzescu's hydrocarbon **2** is a well-known reaction.[1]