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SOLVOLYSES OF DIARYLMETHYL CHLORIDES. A COMPREHENSIVE STABILITY SCALE FOR DIARYLCARBENIUM IONS.

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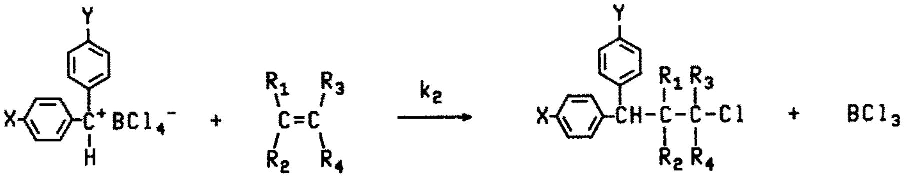
Abstract - Eleven donor substituted diarylmethyl chlorides have been solvolyzed in ethanol. The rate constants, determined at 25°C, and additional ethanolysis data taken from the literature have been connected with solvolysis rate constants, determined in other solvents, to construct a stability scale for 74 diarylcarbenium ions, covering a rate range of $>10^{12}$. Correlation equations are given which allow the calculation of solvolysis rates in other solvents, of equilibrium constants, and of rate constants for reactions involving diarylcarbenium ions.

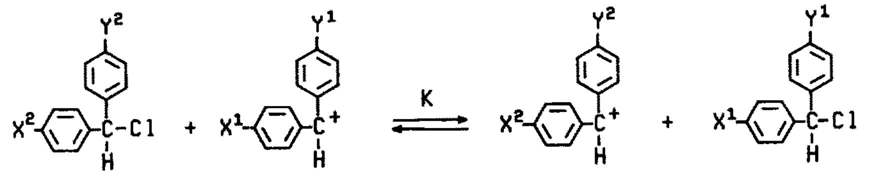
Introduction. The reaction of diarylcarbenium ions 1 with alkenes (eq.1) has been studied as a model reaction[1] for investigating scope and limitations of aliphatic Friedel Crafts alkylations.[2]



(1)

1 2 3

Linear correlations between the reactivities of the ions 1 towards alkenes 2 (lg k_2) and the carbenium ion stabilities defined by the equilibrium constants K were found (eq. 2).[3] It is possible, therefore, to employ linear free enthalpy relationships for the calculation of carbenium ion reactivities from the corresponding equilibrium constants K.



(2)

However, only few values of K are known,[4] and their determination is problematic for less stabilized carbenium ions. In these cases, solvolysis rates appear to be a suitable source for carbenium ion stabilities, since Arnett et al. have shown that the ionization enthalpies of alkyl halides (ΔH_i) determined in superacidic media are linearily correlated with the corresponding solvolysis rate constants.[5]

Numerous solvolytic studies on diarylmethyl derivatives have already been carried out using a variety of conditions,[6-45] and it was the goal of this work to develop a uniform scale of diarylcarbenium ion stabilities, based on the available literature data[6-45] complemented by solvolytic studies carried out in the course of this work.

In ethanol and in solvents of similar ionizing power, diarylmethyl chlorides solvolyze according to a S_N1 mechanism, and only for diarylmethyl derivatives with electron withdrawing substituents and poor leaving groups, nucleophilic assistance by strong nucleophiles has been observed.[36] Since the largest set of kinetic data on benzhydryl chloride solvolyses had been collected in ethanol at 25°C,[19, 9b] we have selected these conditions as standard for our experimental studies and for the envisaged reactivity scale.

Experimental. The diarylmethyl chlorides have been prepared as described previously.[46] Conductimetric rate constants were determined in a 25-mL three necked flask equipped with a thermoelement for temperature control and a Pt plate electrode (cell constant ≈ 96 m^{-1}) connected to a WTW LF 530 conductimeter (4 kHz AC). The experiments were carried out by adding ≈ 150 mg of diarylmethyl chlorides through a septum to 25 mL of ethanol at 25°C (≈ 10^{-2}M solution). In the case of solid diarylmethyl chlorides, solutions in ≈ 100 μL of an inert solvent (CH_2Cl_2) were added. The formation of HCl caused an increase of conductance which was acquired as a function of time using an IBM XT. This curve was connected with a calibration curve, obtained by measuring the conductance during the gradual addition of 3 mL of 0.623 M ethanolic HCl to 100 mL of ethanol, to give a concentration/time correlation which followed a first order rate law.

RESULTS AND DISCUSSION

1. Correlation of Solvolysis Rates in Different Solvents

From the work of Nishida[19] and Baddeley[9] and from our investigations (Tab. 1), a set of 29 solvolysis rate constants (EtOH, 25°C) for para and meta substituted benzhydryl chlorides has become available.[47] Various of these compounds have also been solvolyzed in other solvents, and Fig. 1 and Table 2 show that the log k values determined under different conditions are linearily correlated with each other. With the correlations given in Table 2, it is possible to convert solvolytic data obtained under various conditions to the standard ethanol/25°C. We thus obtain 74 values of k_1 for ethanol/25°C (Table 3).

Table 1. Ethanolysis Rates of <u>para</u> Substituted Diarylmethyl Chlorides (25°C).

X, Y	k_1 / s^{-1}	$\Delta G^{\neq}_{25}$ / kJ mol^{-1}	$\Delta H^{\neq}$ / kJ mol^{-1}	$\Delta S^{\neq}$ / J K^{-1} mol^{-1}
OMe, OMe [a]	57.2	63.0	52.4 ± 0.7	-35.5 ± 3.0
OMe, OPh [a]	15.0	66.3	63.9 ± 0.2	- 8.1 ± 0.7
OMe, Me [a]	5.42	68.8	69.1 ± 0.5	0.7 ± 2.3
OMe, H	0.500	74.7	67.7 ± 0.1	-23.7 ± 0.5
OPh, Me	0.195	77.1	67.9 ± 1.1	-30.5 ± 4.1
OMe, Cl	0.185	77.2	68.5 ± 0.5	-29.1 ± 1.7
OPh, H	0.0222	82.5	71.7 ± 0.9	-36.7 ± 3.1
Me, Me	0.0202	82.7	76.2 ± 0.4	-21.7 ± 1.3
Me, H [b]	0.00123	89.6	85.0 ± 2.6	-15.2 ± 9.1
H, H [c]	$5.34 \cdot 10^{-5}$	97.4		
mes, mes [d,a]	6.77	68.3	65.4 ± 3.1	- 9.7 ± 12.7
xyl, xyl' [e]	0.00522	86.0	80.4 ± 0.3	-18.9 ± 1.1

a) Calculated from activation parameters determined at lower temperatures. b) k_1 / s^{-1} : 0.00124; 0.00123; 0.00123; refs. 7, 9b, 19 c) $k_1/s^{-1} \cdot 10^{-5}$: 5.30; 5.37; 5.39; 5.34; 5.41; refs. 7, 9b, 14, 19, 30. d) Bis(2,4,6-trimethylphenyl)methyl chloride e) (2,4-Dimethylphenyl)(2,5-dimethylphenyl)methyl chloride

The activation parameters of 21 benzhydryl chlorides (Table 1 and Ref. 14, 19, 30) indicate that the changes of reactivitiy caused by variation of the substituents are predominantly due to an alteration of $\Delta H^{\neq}$, not of $\Delta S^{\neq}$. In contrast to a previous statement,[19] the activation entropies are not constant. Though a distinct correlation between rates and $\Delta S^{\neq}$ is not found, it appears as if $\Delta S^{\neq}$ became more negative for less stabilized carbenium ions. Possibly, this trend is caused by stronger solvation of the less stabilized carbenium ions.

Table 2. Correlation between Ethanolysis Rates (25°C) of Diarylmethyl Chlorides (k_1) with Solvolysis Rates in other Solvents (k').

	Correlation	Solvent	Temperature	Number of Values	r	Ref.
(1)	$\lg(k_1) = 1.0637 \lg(k') + 1.3134$	90% acetone	25°C	4	.9997	/13/
(2)^{a}	$\lg(k_1) = .8996 \lg(k')_r - .1995$	85% acetone	0°C	11	.9988	/18/
(3)	$\lg(k_1) = .9441 \lg(k') - .3409$	80% acetone	25°C	8	.9990	/7,13,40,42/
(4)	$\lg(k_1) = .9155 \lg(k') + .8668$	80% acetone	0°C	5	.9990	/7,12,13,16/
(5)	$\lg(k_1) = .8654 \lg(k') - 1.4070$	70% acetone	25°C	4	.9999	/15/
(6)	$\lg(k_1) = .9266 \lg(k') + .1187$	70% acetone	0°C	8	.9993	/12,15,33d/
(7)	$\lg(k_1) = .9234 \lg(k') - .1405$	66.7% acetone	0°C	5	.9954	/12/
(8)	$\lg(k_1) = .9210 \lg(k') + .0716$	90% EtOH	0°C	4	.9992	/12,16,40d/
(9)	$\lg(k_1) = 1.0966 \lg(k') - .6243$	90% EtOH	25°C	3	.9960	/16,40d/
(10)	$\lg(k_1) = 1.0414 \lg(k') - 1.4230$	80% EtOH	25°C	4	.9965	/16,40d/
(11)	$\lg(k_1) = 1.0075 \lg(k') + .5914$	9/1 EtOH/Me_2CO	25°C	7	.9967	/23/
(12)	$\lg(k_1) = 1.0607 \lg(k') + 1.3026$	^{i}PrOH	25°C	21	.9991	/19/
(13)	$\lg(k_1) = .9859 \lg(k') - 1.2399$	MeOH	25°C	28	.9993	/19/
(14)^{b}	$\lg(k_1) = 1.2803 \lg(k') + 4.1177$	90% acetone	99.5°C	4	.9999	/35e/
(15)^{b}	$\lg(k_1) = 1.3488 \lg(k') + 2.0365$	75% acetone	114.6°C	6	.9988	/17/
(16)^{b}	$\lg(k_1) = 1.2719 \lg(k') + 1.3460$	80% EtOH	100°C	6	.9994	/21/
(17)^{b}	$\lg(k_1) = 1.2687 \lg(k') + 0.8643$	70% EtOH	100°C	6	.9992	/21/
(18)^{b}	$\lg(k_1) = 1.2938 \lg(k') + 0.5794$	60% EtOH	100°C	6	.9999	/21/
(19)^{b}	$\lg(k_1) = 1.2997 \lg(k') + 0.2013$	50% EtOH	100°C	6	.9999	/21/

a) $\lg(k')_r$ are relative rate constants with $(k')_{r,1\text{-OMe},H} = 1$.
b) k' of p-nitrobenzoates

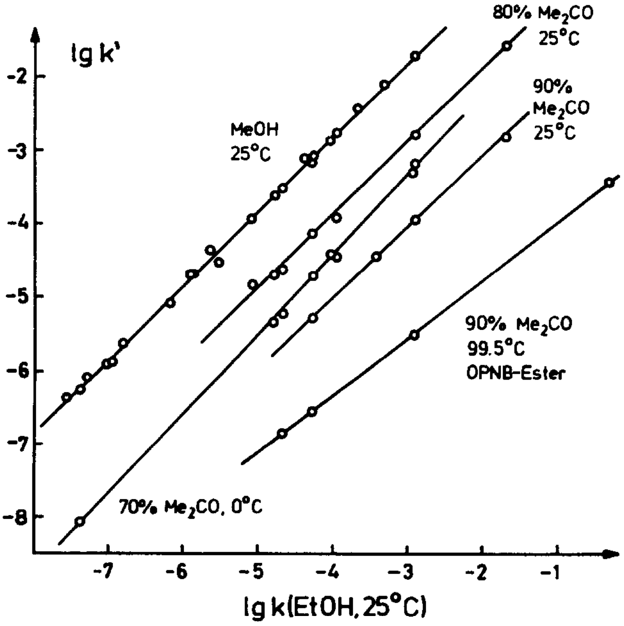


Figure 1. Correlations of Solvolysis Rates of Diarylmethyl Derivatives in Various Solvents.

Table 3. Ethanolysis Rates of Diarylmethyl Chlorides (25°C) and Calculated Ionization Free Enthalpies $\Delta G_i°$ in CH_2Cl_2/BCl_3 at -70°C.

No.	X, Y	$\lg(k_1)$	ref.	correlation[a]	$\Delta G_i°(CH_2Cl_2, BCl_3, -70°C)$ [b]
para Substituents:					
1	NO_2, NO_2	-10.739	/18/	2	62.4[c]
2	NO_2, Cl	-7.565	/18/	2	38.1
3	NO_2, H	-7.373	/19/	-	36.6
4	CN, H	-7.007	/19/	-	33.8
5	NO_2, F	-6.703	/18/	2	31.5
6	NO_2, Ph	-6.064[d]	/18, 33d/	2, 6	26.6
7	NO_2, ^{t}Bu	-5.961	/18/	2	25.8
8	NO_2, Me	-5.527	/18/	2	22.5
9	Br, Br	-5.303	/13c/	3	20.8
10	Cl, Cl	-5.093	/19/	-	19.2
11	Br, H	-4.793	/19/	-	16.9
12	I, H	-4.767[d]	/15/	5, 6	16.7
13	NO_2, An	-4.746	/18/	2	16.5
14	Cl, H	-4.686	/19/	-	16.0
15	H, H	-4.271	/7,9b,14,19,30/	-	12.9
16	F, H	-4.032	/19/	-	11.0
17	NO_2, OPh	-3.901	/18/	2	10.0
18	3,4-C_4H_4, H	-3.562	/13b/	1	7.4
19	2,3-C_4H_4, H	-3.432[d]	/6, 13b, 14/	1	6.5
20	Ph, H	-3.377[d]	/6,14,18,20,33d/	2, 6, 13	6.0
21	Cl, Me	-3.305	/19/	-	5.5
22	^{t}Bu, H	-3.151[d]	/7, 12, 13c, 18/	1, 2, 4, 6, 7	4.3
23	$^{t}BuCH_2$, H	-3.088[d]	/9b, 12/	2, 6	3.8
24	^{i}Bu, H	-3.063[d]	/9b, 12/	4, 6	3.6
25	^{i}Pr, H	-3.048[d]	/7, 12, 14/	3, 4, 6, 8	3.5
26	^{n}Pr, H	-3.020[d]	/12/	4, 6	3.3
27	Et, H	-2.938[d]	/6, 7, 8a, 9, 12/	3, 4, 8	2.7
28	cHexyl, H	-2.914	/9c/	-	2.5
29	Me, H	-2.910	/this work,7,9b,19/	-	2.5 (3.0)
30	cPentyl, H	-2.842	/9c/	-	1.9
31	An, H[e]	-2.600	/18/	2	0.1
32	^{t}Bu, ^{t}Bu	-2.146[d]	/13, 16/	1	- 3.4
33	OMe, NO_2	-2.053[f]	/18/	2	- 4.1
34	Me, Me	-1.694	this work	-	- 6.8 (- 7.0)
35	OPh, H	-1.654	this work	-	- 7.2 (- 9.2)
36	OMe, Cl	-0.733	this work	-	-14.2 (-14.2)
37	OPh, Me	-0.710	this work	-	-14.4 (-15.4)
38	OMe, H	-0.301	this work	-	-17.5 (-16.6)
39	OMe, F	-0.098	/18/	2	-19.1
40	OMe, Ph	.236	/18/	2	-21.6
41	OMe, ^{t}Bu	.404	/18/	2	-22.9
42	OMe, An[e]	.712[d]	/18, 33d/	2, 6	-25.2
43	OMe, Me	.734	this work	-	-25.4 (-22.8)
44	OMe, OPh	1.177	this work	-	-28.8 (-27.9)
45	OMe, OMe	1.758	this work	-	-33.2 (-35.1)
meta Substituents:					
46	Cl, Cl	-7.273	/19/	-	35.8
47	NO_2, H	-6.954	/19/	-	33.4
48	CN, H	-6.796	/19/	-	32.2
49	Cl, H	-5.910	/14, 19/	-	25.4
50	Br, H	-5.893	/14, 19/	-	25.3
51	F, H	-5.760	/19/	-	24.3
52	Ph, H	-4.521	/20/	13	14.8
53	OMe, H	-4.292	/19/	-	13.0
54	OEt, H	-4.191	/10/	12	12.3
55	^{i}Pr, H	-4.098[d]	/13a, b/	3, 4	11.5
56	Et, H	-4.083[d]	/13a, b/	3, 4	11.4
57	^{t}Bu, H	-4.040[d]	/12, 13b, 16/	4, 6, 7, 8	11.1
58	Me, H	-3.953	/19/	-	10.4
59	Me, Me	-3.658	/19/	-	8.1

Miscellaneous Substitutions[g]:

60	mCl, mCl, p'Cl	-7.556	/19/	-	38.0
61	mCl, p'Cl	-6.298	/10, 19/	12	28.4
62	mCl, mCl, p'Me	-5.654	/19/	-	23.5
63	mCl, p'Me	-4.370	/19/	-	13.6
64	oMe, o'Me	-3.899	/23/	11	10.0
65	mMe, mMe	-3.766[d]	/16/	3, 8	9.0
66	m^tBu, m^tBu	-3.742[d]	/16/	3, 8	8.8
67	mMe, mMe, p^iPr	-2.824	/9b/	-	1.8
68	mMe, mMe, pEt	-2.782	/9b/	-	1.5
69	mMe, mMe, pMe	-2.745	/9b/	-	1.2
70	mMe, p'Me	-2.629	/19/	-	0.3
71	mCl, mCl, p'OMe	-2.428	/19/	-	- 1.2
72	xyl, xyl'	-2.282	this work	-	- 2.3
73	mCl, p'OMe	-1.432	/19/	-	- 8.8
74	mes, mes	0.831	this work	-	-26.2

a) Correlation used for the calculation of k_1; numbers refer to Table 2. b) Ionization free enthalpy $\Delta G_i°$ for the reaction $Ar_2CHCl + BCl_3 \rightarrow Ar_2CH^+ BCl_4^-$ at -70°C in CH_2Cl_2 according to eq. (5); experimental values /4/ in parentheses. c) Unreliable value due to possible nucleophilic assistance in the solvolysis reaction. d) Averaged from various sources. e) An = 4-methoxyphenyl. f) k_1 appears to be too high based on a σ^+ correlation. g) Further solvolysis rates of diarylmethyl chlorides with condensed benzenoid rings ref. /13b/; cycloalkyl annelated compounds, ref. /8, 9a, c/; ortho-methyl substituted compounds, ref. /22, 23/.

2. Correlation with Ionization Free Enthalpies - Carbenium Ion Character of the Solvolysis Transition States

The ionization enthalpies of secondary and tertiary alkyl- and arylalkyl chlorides in SO_2ClF/SbF_5 have been reported to be correlated (eq. 3) with their ethanolysis rate constants at 25°C.[5,48]

$$\Delta H_i(RCl,\ SO_2ClF/SbF_5) = 6.78 \cdot \lg k_1 - 157\ [kJ/mol] \qquad (3)$$

A similar correlation (eq. 4) can be derived for the ionization of the corresponding alcohols in Magic Acid / SO_2ClF.[48]

$$\Delta H_{rxn}(ROH,\ SO_2ClF/SbF_5/FSO_3H) = 6.99 \cdot \lg k_1 - 202\ [kJ/mol] \qquad (4)$$

When the ethanolysis rate constants in eqs. (3) and (4) are substituted by the corresponding activation free enthalpies, correlations $\Delta G^{\neq}/\Delta H_i$ and $\Delta G^{\neq}/\Delta H_{rxn}$ are obtained, the slopes of which (0.84 and 0.82) have been interpreted to indicate that 82 - 84% of the carbenium ion character is developed in the solvolysis transition states.[5,48,49]

In analogy to this $\Delta G^{\neq}/\Delta H_i$ relationship, a rate/equilibrium relationship is found for the ionization of benzhydryl chlorides. According to eq. 5, the logarithms of the ethanolysis rate constants (25°C) are linearily correlated with the ionization free enthalpies in CH_2Cl_2/BCl_3[4] (9 values, r = 0.992).

$$\Delta G_i°(CH_2Cl_2/BCl_3,\ -70°C) = -\ 7.65\ \lg k_1 - 19.8\ [kJ/mol] \qquad (5)$$

When k_1 is substituted by $\Delta G^{\neq}_{solv}$, eq. 5 can be rewritten to give

$$\Delta G^{\neq}_{solv}(EtOH,\ 25°C) = 0.746 \cdot \Delta G_i°(BCl_3/CH_2Cl_2,\ -70°C) + 87.8\ [kJ/mol] \qquad (6)$$

The slope of this linear free enthalpy relationship (Figure 2) indicates that ≈ 75% of carbenium ion character is developed in the ethanolysis transition states.

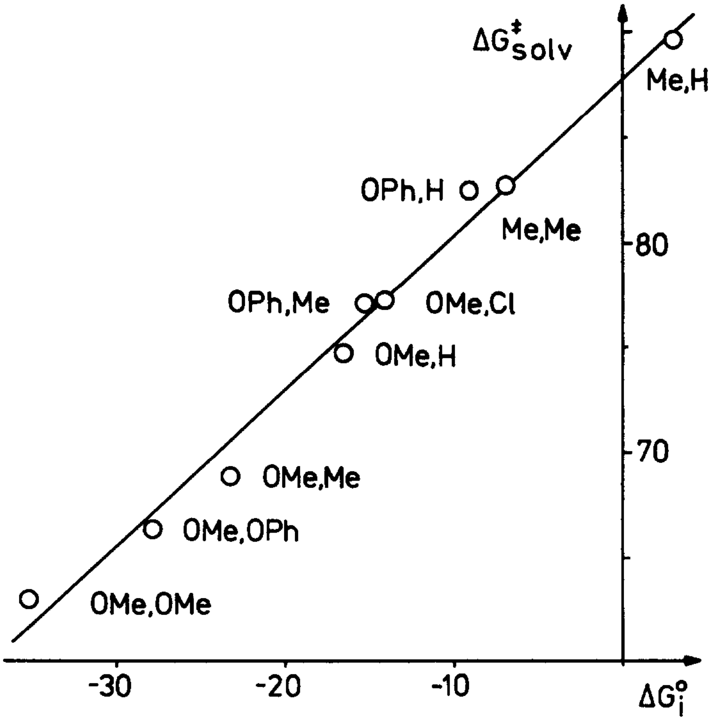


Figure 2. Correlation of $\Delta G_i°(Ar_2CHCl + BCl_3 \rightleftharpoons Ar_2CH^+BCl_4^- /CH_2Cl_2, -70°C)$ with $\Delta G^{\neq}$ of the Corresponding Ethanolysis Reactions (25°C).

Since the carbenium ion stabilities ($\Delta G_i°$, CH_2Cl_2/BCl_3) are of importance for our reactivity discussions,[1] eq. 5 has been used to convert all solvolysis rate constants listed in Table 3 into $\Delta G_i°$ values (Table 3, right column).

Diarylcarbenium ion stabilities have also been derived from ionization equilibria determined in sulfuric acid, and the resulting pK_{R^+} values[50] are correlated with the ethanolysis rate constants of Table 3 by eq. 7 (14 values, r = 0.9971).[51]

$$pK_{R^+} = 1.26 \cdot \lg k_1 - 7.79 \qquad (7)$$

Multiplication of eq. 7 with - 2.303 RT converts pK_{R^+} into a free enthalpy term, and, as expected, the resulting slope (- 7.20) closely resembles that of eq. 5.

3. Correlations with σ^+ Parameters

The reactivities of multiply substituted systems are usually not strictly correlated with the σ^+-parameters, which have been derived from solvolyses of substituted cumyl chlorides.[18,19,52,53] σ^+-Parameters are available for 58 compounds of Table 3,[54] and Fig. 3 shows a moderately linear correlation between the ethanolysis rate constants and $\Sigma\sigma^+$ (r = 0.982). As reported by Nishida,[19] the largest deviations arise for compounds, in which one aryl ring is substituted by strongly electron withdrawing substituents while the other is bearing electron releasing substituents. If compounds with $\Delta\sigma^+ > 1.2$ (difference of σ^+ for the two aryl groups) are disregarded, a correlation for 54 substrates results (eq. 8, r = 0.995), which covers a reactivity range greater 10^{12}.[55]

$$\lg k_1 = - 4.117\ \Sigma\sigma^+ - 4.064 \qquad (8)$$

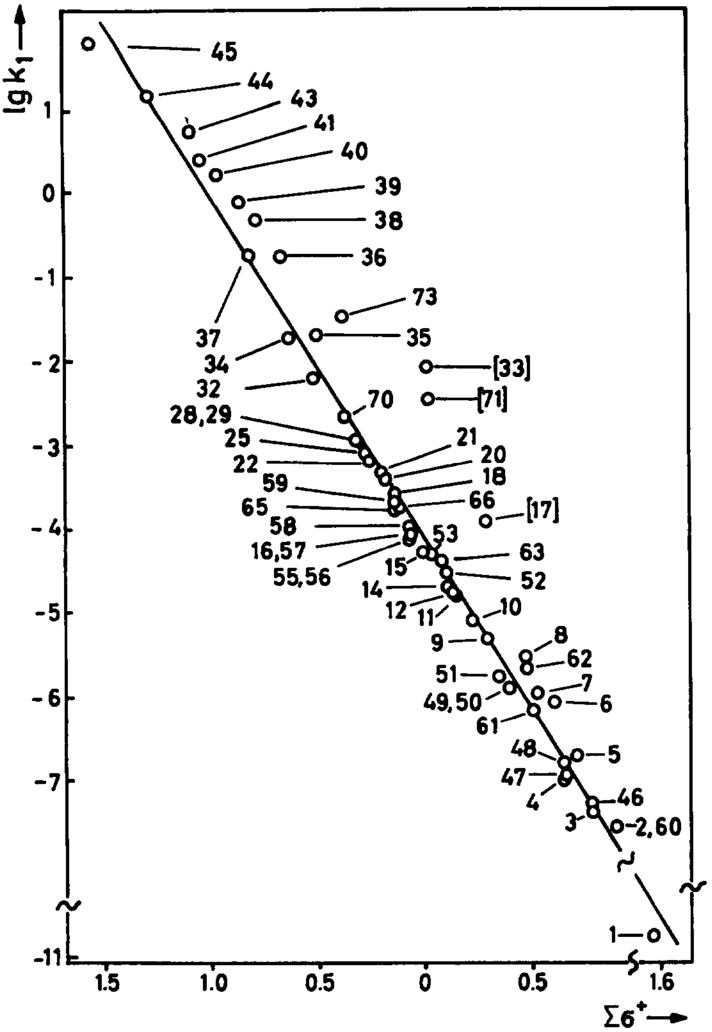


Figure 3. Correlation of the Ethanolysis Rate Constants (25°C) of Diarylmethyl Chlorides with σ⁺-Parameters (points No. 17, 33, and 71 omitted from correlation).

4. Correlations with Carbenium Ion Reactivities

Additions of nucleophiles to carbenium ions also follow rate equilibrium relationships[45], and, consequently, they are linearly correlated with solvolysis rates. McClelland and Steenken determined the reactivity of water towards diarylcarbenium ions, generated by LASER flash photolysis in 20% aqueous acetonitrile.[52] The resulting second order rate constants (k_s, CH_3CN : H_2O = 80 : 20, v/v, 20°C) and the ethanolysis rate constants of Table 3 are correlated by eq. 9 (8 values, r = 0.983, Fig. 4).

$$\lg k_s = - 0.632 \lg k_1 + 6.220 \qquad (9)$$

The slower reactions of diarylcarbenium tetrachloroborates with 2-methyl-1-pentene in CH_2Cl_2 at -70°C ($\lg k_2$) follow a linear correlation with considerably more negative slope (eq. 10),[1a] which indicates that the reactions with alkenes are characterized by a later transition state (7 values, r = 0.972)

$$\lg k_2 = - 1.265 \lg k_1 + 0.896 \qquad (10)$$

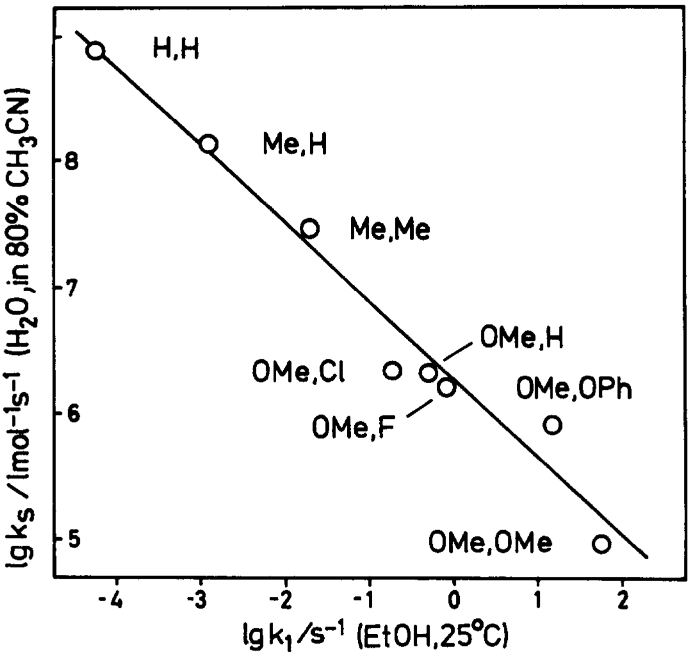


Figure 4. Correlation of the Reactivities of Diarylcarbenium Ions with Water in 80% Acetonitrile (20°C) with the Ethanolysis Rate Constants (25°C) of the Corresponding Diarylmethyl Chlorides.

Conclusion. With a list of 74 compounds, Table 3 represents the most comprehensive scale of diarylcarbenium ion solvolysis rate constants presently available. Since the solvolysis rate constants are connected with equilibrium constants by linear free enthalpy relationships, this list is equivalent to a stability scale for diarylcarbenium ions. Linear free enthalpy relationships have been found to correlate solvolysis rates of benzhydryl chlorides with diarylcarbenium ion reactivities towards nucleophiles (water and 2-methyl-1-pentene). As previous work has demonstrated the existence of linear reactivity-reactivity relationships for reactions of diarylcarbenium ions with various alkenes[1d], the data of Table 3 allow the prediction of rate constants for reactions of diarylcarbenium ions with a large variety of nucleophiles, which will be treated in successive publications.

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