The Solvolysis of Furylmethylcarbinol Derivatives[1]

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A kinetic study of the solvolysis of a series of furylmethylcarbinyl *p*-nitrobenzoates has been carried out. Substituents in the 5 position exert a profound influence on the rate of solvolysis. Results for six different substituents are satisfactorily correlated by Brown's σ^+ substituent constants with ρ −7.5, one of the most negative values for ρ observed in the correlation of solvolysis reactions.

The sensitivity of furan to attack by electrophilic reagents is well known, and is the result of the relatively small resonance energy of the furan ring, coupled with the stabilizing influence of the heteroatom for a positive charge.[3] Recently several studies have been carried out with the purpose of comparing furan with benzene and other aromatic systems. Marino and his coworkers have compared the rates of bromination of furan and benzene[4] and also the rates of trifluoroacetylation.[5] They showed that furan is 10^{11} more reactive than benzene in bromination, and that generally similar results obtained in the trifluoroacetylation.[6] Electrophilic hydrogen deuterium exchange in furan has been investigated. In a preliminary communication by Schwetlik, Unverferth and Meyer,[7] rates of dedeuteration by sulfuric acid have been reported, showing the very high reactivity of furan. However, these studies are attended with severe difficulty, as the furan ring is known to open readily in acid to 1,4-dicarbonyl compounds.[8,9] Other studies have involved replacement of other groups on the furan ring. Demercuration[10] and replacement of the trimethylsilyl group by hydrogen[11] have been investigated. In all of these studies the high reactivity is apparent, and a generally satisfactory correlation may be noted.

An alternative approach to the study of aromatic reactivity is the investigation of the rate of solvolysis of appropriate arylmethyl compounds. Benzyl systems as probes for the properties of the corresponding aromatic hydrocarbon have been studied by Streitwieser, Jagow and Williams,[12] by Fierens, *et al.*,[13] and by Dewar and Sampson.[14] This is the approach we have used in the present investigation. The advantages of such an approach are that the reactivity of furan derivatives may be studied in a neutral environment.

At the time this study was initiated there were few such studies reported. The rate of solvolysis of furfuryl chloride in 70–90% dioxane had been measured by Egyed and Gerecs,[15] and it can be estimated from this study that furfuryl chloride is about 10 times more reactive than *p*-methoxybenzyl chloride.[16] Braude and Fawcett[17] noted briefly the similarity of a furan moiety and an anisyl moiety in promoting the acid-catalyzed rearrangement of cinnamyl alcohols. More recently two additional reports have appeared. Gal'bershtam, Khachaturova, Novitskii and Yur'ev[18] report that 5-nitro-2-chloromethylfuran is much less reactive than furfuryl chloride in methanol. Dalrymple and White[19] have compared the reactivity of chloromethyl derivatives of furan, benzofuran and dibenzofuran with molecular orbital calculations.

Experimental Section[20]

5-Methyl-2-acetylfuran was prepared from 2-methylfuran by the method of Farrar and Levine[21] in 36% yield, bp 60° (5 mm), [lit.[21] bp 71–73° (8 mm)].

5-Bromo-2-acetylfuran was prepared from 2-bromofuran[22] by the method of Nazarova, Babaev and Natal'ina[23] in 56% yield, mp 94° (lit.[23] mp 95–96°).

4,5-Dibromo-2-acetylfuran was prepared from 2-acetylfuran by the method of Gol'dfarb and Tarasova[24] in 55% yield, mp 55–56° (lit.[24] mp 54.5–55.5°).

4-Bromo-2-acetylfuran was prepared from 4,5-dibromo-2-acetylfuran by the method of Gol'dfarb and Tarasova[25] in 80% yield, mp 66–68° (lit.[25] mp 68°).

5-Carbethoxy-2-acetylfuran was prepared according to the procedure of Gilman and Calloway.[26] To a stirred solution of stannic chloride (200 ml, 444 g, 1.70 mol) in 200 ml of benzene cooled in an ice water bath was added ethyl 2-furoate (44.4 g, 0.32 mol) and acetic anhydride (32.6 g, 0.32 mol) at a rate to maintain the temperature below 5°. The solution was refluxed overnight, cooled to room temperature, and then poured over ice. Benzene, 500 ml, was added and the organic layer was washed with a saturated solution of sodium bicarbonate and with water. After removing the benzene on a rotary evaporator, the residue was distilled. The fraction boiling at 125–175° (15 mm) was collected. The distillate solidified and was recrystal-

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TABLE I

NMR CHEMICAL SHIFTS[a] AND COUPLING CONSTANTS[b] OF 2-FURYLMETHYLCARBINOLS

Compound	Registry no.	Solvent	δ						Additional data
			H_3	H_4	H_5	CH_3	CH	OH[c]	
Unsubstituted	4208-64-4	CCl_4	6.10 (m)[d]	6.10 (m)	7.20 (m)	1.36 (d)	4.68 (q)	4.22 (s)	$J_{CH_3CH} = 7$
α-Deuterio	18753-47-4	$CDCl_3$	6.20 (m)	6.20 (m)	7.28 (m)	1.45 (s)		3.25 (s)	
5-Methyl	14003-15-7	$CDCl_3$	6.05 (d)	5.82 (d)		1.40 (d)	4.72 (q)	3.62 (s)	$J_{3,4} = 4$; $J_{CH_3CH} = 7$; 5-CH_3, δ 2.21 (s)
5-Bromo	18753-49-6	CCl_4	6.10 (m)	6.10 (m)		1.38 (d)	4.68 (q)	4.29 (s)	$J_{CH_3CH} = 7$
5-Nitro	18753-50-9	$CDCl_3$	6.59 (d)	7.33 (d)		1.59 (d)	4.97 (q)	3.90 (s)	$J_{3,4} = 4$; $J_{CH_3CH} = 7$
5-Carbethoxy	18743-92-5	$CDCl_3$	6.29 (d)	7.02 (d)		1.52 (d)	4.68 (q)	4.40 (s)	$J_{3,4} = 4$; $J_{CH_3CH} = 7$; $CH_2C\mathbf{H}_3$, δ 1.31 (t); $C\mathbf{H}_2CH_3$, δ 4.28 (q); $J_{CH_3CH_2} = 7$
4-Bromo	18743-93-6	$CDCl_3$	6.20 (d)		7.30 (d)	1.42 (d)	4.65 (q)	3.83 (s)	$J_{3,5} = 1$; $J_{CH_3CH} = 7$
4-Carbethoxy	18743-94-7	$CDCl_3$	6.48 (d)		7.82 (d)	1.49 (d)	4.79 (q)	3.73 (s)	$J_{3,5} = 1$; $J_{CH_3CH} = 7$; $CH_2C\mathbf{H}_3$, δ 1.31 (t); $C\mathbf{H}_2CH_3$, δ 4.23 (q); $J_{CH_3CH_2} = 7$

[a] δ values are in parts per million from internal TMS. [b] J is the observed coupling constant in cycles per second. [c] Chemical shifts are highly dependent upon concentration. [d] Multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

TABLE II

MELTING POINTS AND ELEMENTAL ANALYSES FOR 2-FURYLMETHYLCARBINYL *p*-NITROBENZOATES

Compound	Registry no.	Mp, °C	Calcd, %			Found, %		
			C	H	N	C	H	N
Unsubstituted	18743-95-8	41.5–42.5	59.77	4.24	5.36	59.97	4.28	5.58
5-Methyl	18743-96-9	62.0–63.0	61.09	4.76	5.09	61.10	4.77	5.07
5-Bromo[a]	18743-97-0	80.5–81.5	45.90	2.96	4.12	45.71	2.98	4.20
5-Nitro	18749-92-3	149.5–150.5	50.98	3.29	9.15	50.77	3.03	8.97
5-Carbethoxy	18743-98-1	86.0–87.0	57.66	4.54	4.20	57.87	4.52	4.30
4-Bromo[b]	18743-99-2	68.0–69.0	45.90	2.96	4.12	45.67	3.08	4.09
4-Carbethoxy	18744-00-8	114.0–115.0	57.66	4.54	4.20	57.67	4.71	4.28

[a] Calcd for Br: 23.49. Found: 23.48. [b] Calcd for Br: 23.49. Found: 23.70.

lized from ethanol yielding 8.4 g (14%) of 5-carbethoxy-2-acetylfuran, mp 82–86° (lit.[26] 95–86°, 20%). Although the nmr spectrum is consistent with that expected for the desired compound, the melting range indicates some impurity. A small amount of the 2,4 isomer may well be present.[27,28] The carbinol prepared by reduction with sodium borohydride in ethanol showed no contamination with the 2,4 isomer upon close examination of the nmr spectrum (see below).

4-Carbethoxy-2-acetylfuran was prepared from ethyl 3-furoate using the procedure of Eugster and Waser,[29] who prepared the methyl ester.

A mixture of ethyl 3-furoate (12.4 g) and acetic anhydride (10.2 g) was heated to 50°, then boron trifluoride etherate (2 ml) was added all at once. The solution was heated to 100° with stirring. After the exothermic reaction had subsided, water was added, and the material worked up in the usual manner. Distillation afforded much recovered ethyl 3-furoate, and a satisfactory yield of 4-carbethoxy-2-acetylfuran, mp 76–77°. The infrared spectrum in chloroform showed bands at 3000 (s), 1710 (s), 1580 (s), and 1500 cm^{-1} (s).

Anal. Calcd for $C_9H_{10}O_4$: C, 59.33; H, 5.53. Found: C, 59.39; H, 5.69.

5-Nitro-2-acetylfuran was prepared from 2-acetylfuran (18 g) and acetyl nitrate by the method of Rinkes,[30] in 24% yield, mp 78–79° (lit.[30] mp 78.5°).

2-Furylmethylcarbinols were prepared by reducing the ketones with sodium borohydride in anhydrous methanol. Sodium borohydride was added in portions to a stirred solution of the ketone in methanol, keeping the temperature below 40°. After all the reagent had been added, the reaction solution was stirred for 1 hr at room temperature. The methanol solution was poured into water (five parts water to one part methanol) and extracted into ether. The ether solution was dried over anhydrous magnesium sulfate and filtered. Removal of the solvent on a rotary evaporator generally yielded >90% of the carbinol.

In the work-up of the 5-nitro, 5-carbethoxy, 4-carbethoxy, and 4-bromo compounds, the water was made slightly acidic before the methanol solution was added. The other compounds, which are more acid sensitive, were worked up using water without added acid.

The 4- and 5-carbethoxy compounds were reduced in anhydrous ethanol instead of methanol to avoid transesterification. All the carbinols were characterized by nmr (Table I).

α-Deuterio-2-furylmethylcarbinol.—Lithium aluminum deuteride (>98% D, 2.00 g) in 250 ml of anhydrous ether was stirred while 2-acetylfuran (5.00 g) dissolved in 50 ml of ether was added over a period of 20 min. After the addition was complete, the mixture was refluxed for 1.5 hr. The reaction flask was then cooled in an ice water bath, and the solution was treated with 10 ml of water and 5 ml of saturated ammonium chloride. The ether layer was decanted, and two 25-ml portions of ether were used to extract the precipitated material. The combined ether solutions were washed with water, dried over anhydrous magnesium sulfate, and filtered. Removal of the ether on a rotary evaporator yielded 4.9 g (95%) of α-deuterio-2-furylmethylcarbinol. The nmr spectrum in deuteriochloroform was the same as that observed for the undeuterated alcohol except that the methine resonance at δ 4.7 was absent and the methyl resonance at δ 1.4 was a singlet.

2-Furylmethylcarbinyl *p*-Nitrobenzoates.—The appropriate 2-furylmethylcarbinol dissolved in 50 ml of pyridine was cooled in an ice water bath and stirred while freshly recrystallized *p*-nitrobenzoyl chloride was added at a rate to maintain the temperature below 20°. The reaction mixture was stirred for 0.5 hr in the ice bath and an additional 1 hr at room temperature. The mixture was then poured into a beaker containing 150 ml of ice water whereupon the product crystallized. Filtration and recrystallization from hot hexane or hexane–ethyl acetate mixtures gave pure esters in good yields. Relevant data on the *p*-nitrobenzoate are given in Tables II and III.

5-Carbethoxy-2-furylmethylcarbinyl Chloride.—5-Carbethoxy-2-furylmethylcarbinol was converted into its chloride

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TABLE III

NMR CHEMICAL SHIFTS[a] AND COUPLING CONSTANTS[b] OF 2-FURYLMETHYLCARBINYL *p*-NITROBENZOATES

		δ						
Compound	Solvent	H_3	H_4	H_5	CH_3	CH	C_6H_4	Additional data
Unsubstituted	CCl_4	6.32 (m)[c]	6.32 (m)	7.34 (m)	1.72 (d)	6.14 (q)	8.13 (s)	$J_{CH_3CH} = 7$
α-Deuterio	CCl_4	6.33 (m)	6.33 (m)	7.34 (m)	1.71 (s)		8.12 (s)	
5-Methyl	CCl_4	6.22 (d)	6.22 (d)		1.70 (d)	6.12 (q)	8.18 (s)	$J_{3,4} = 4$; $J_{CH_3CH} = 7$; 5-CH_3, δ 2.30 (s)
5-Bromo	CCl_4	6.43 (d)	6.28 (d)		1.77 (d)	6.12 (q)	8.23 (s)	$J_{3,4} = 4$; $J_{CH_3CH} = 7$
5-Nitro	$CDCl_3$	6.80 (d)	7.32 (d)		1.82 (d)	6.27 (q)	8.26 (s)	$J_{3,4} = 4$; $J_{CH_3CH} = 7$
5-Carbethoxy	$CDCl_3$	6.50 (d)	7.09 (d)		1.81 (d)	6.20 (q)	8.20 (s)	$J_{3,4} = 4$; $J_{CH_3CH} = 7$; $CH_2\mathbf{CH_3}$, δ 1.36 (t); $\mathbf{CH_2}CH_3$, δ 4.35 (q); $J_{CH_3CH_2} = 7$
4-Bromo	CCl_4	6.10 (d)		6.98 (d)	1.62 (d)	5.80 (q)	7.74 (s)	$J_{3,5} = 1$; $J_{CH_3CH} = 7$
4-Carbethoxy	$CDCl_3$	6.81 (d)		7.97 (d)	1.78 (d)	6.23 (q)	8.22 (s)	$J_{3,5} = 1$; $J_{CH_3CH} = 7$; $CH_2\mathbf{CH_3}$, δ 1.33 (t); $\mathbf{CH_2}CH_3$, δ 4.31 (q); $J_{CH_3CH_2} = 7$

[a] δ values are in parts per million from internal TMS. [b] *J* is the observed coupling constant in cycles per second. [c] Multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

according to the procedure of Brown and Rei[31] using an automatic hydrogenator[32] to regulate hydrogen chloride generation from hydrochloric acid and sulfuric acid. A solution of 5-carbethoxy-2-furylmethylcarbinol (2.02 g) in 10 ml of carbon tetrachloride immediately took up 1.23 equiv of hydrogen chloride and then no more (lit.[31] 1.35 equiv taken up at 0°). After 3 min, the reaction flask was removed from the apparatus. The water which had formed was removed, and the carbon tetrachloride solution was dried over anhydrous sodium sulfate and then filtered. Removal of the solvent on a rotary evaporator yielded 2.20 g (99%) of the chloride, which was purified by molecular distillation (35°, 0.01 mm). The infrared spectrum of the neat compound showed bands at 3000 (m), 1725 (s), 1590 (m), 1525 (m), 770 cm^{-1} (s).

Anal. Calcd for $C_9H_{11}ClO_3$: C, 53.34; H, 5.47; Cl, 17.50 Found: C, 53.32; H, 5.29; Cl, 17.29.

5-Nitro-2-furylmethylcarbinyl Chloride.—To 5-nitro-2-furylmethylcarbinol (1.58 g) was added 20 ml of refrigerated thionyl chloride. The solution was stirred at room temperature for 3 hr and then poured into ice. The brown oil which separated was extracted into pentane and washed with aqueous sodium bicarbonate and water. Removal of the solvent on a rotary evaporator yielded 1.20 g (68%) of 5-nitro-2-furylmethylcarbinyl chloride as a yellow oil. The product was purified by molecular distillation (40°, 0.005 mm). The infrared spectrum of the neat chloride showed bands at 3100 (m), 2900 (m), 1590 (m), 1500 (s), 740 cm^{-1} (s). The nmr spectrum of the product in deuteriochloroform showed *ca.* 7% of the alcohol remaining.

This alcohol was too unreactive to be converted into the chloride using the more convenient method employing hydrogen chloride gas.

2-Vinylfuran was prepared from 2-furanacrylic acid by the method of Moureu, Dufraisse and Johnson.[33] Spectral data were gathered immediately. The olefin polymerized within 48 hr. The infrared spectrum of the neat compound showed bands at 3100 (m), 1640 (s), 1550 (m), 1480 (s), and 885 cm^{-1} (m). The nmr spectrum in carbon tetrachloride showed multiplets for the furan ring protons at δ 7.20 (1 H) and 6.15 (2 H). The terminal vinyl protons showed multiplets at δ 5.06 (1 H), 5.56 (1 H), and 6.30 (1 H); λ_{max} 263 (log ε = ~4.0) (80% ethanol) [lit.[33] λ_{max} 260, log ε = 4.2 (ethanol)].

2-Furylmethylcarbinyl ethyl ether was isolated from the solvolysis of 2-furylmethylcarbinyl *p*-nitrobenzoate in 80% aqueous ethanol. A dichloromethane solution of the neutral products was washed with copious amounts of water to remove the 2-furylmethylcarbinol, which is more soluble in water than the ether. A vpc trace of a concentrated dichloromethane solution showed only one peak with a retention time identical with that of the more abundant compound in the product mixture. The nmr spectrum of the ether in deuteriochloroform showed multiplets for the furan ring protons at 7.35 (1 H) and 6.29 (2 H). Quartets were present at 4.50, *J* = 7 cps (1 H), and 3.46 *J* = 7 cps (2 H). Resonances for the methyl groups adjacent to the methine group and the methylene group showed a doublet at δ 1.48, *J* = 7 cps (3 H), and a triplet at 1.17, *J* = 7 cps (3 H), respectively.

Product Analysis.—Analysis of the products from the solvolysis of 2-furylmethylcarbinyl *p*-nitrobenzoate in 80% aqueous ethanol at 45° was carried out according to the vpc procedure of Buckson and Smith,[34] who analyzed the ethanolysis products from phenyldimethylcarbinyl chloride and *p*-nitrobenzoate. Additional confirmatory data was provided by nmr spectroscopy.

2-Furylmethylcarbinyl *p*-nitrobenzoate (0.01 *M*) in 80% ethanol was solvolyzed at 45° for 1000 min, *ca.* 10 half-lives. The solution was diluted with water and extracted with six 50-ml portions of dichloromethane. The combined organic extracts were washed with 50 ml of saturated sodium bicarbonate solution and 50 ml of water. After drying over anhydrous magnesium sulfate, the solution was filtered and then concentrated to *ca.* 5 ml by distilling the solvent through a 6-in. Vigreux column.

A 10-μl sample of the remaining solution was injected into an Aerograph A90-P gas chromatograph equipped with a 20% SE-30 on Chromosorb W column. The column and the injection port were kept at 62 and 112°, respectively. Working at low temperature is necessary to avoid decomposition of the products in the instrument. Only two peaks with areas in the ratio of 1:6 were observed. The molar responses of the ether and the alcohol relative to that of chlorobenzene, a convenient standard, were determined in separate experiments. After making the correction for the response difference, the ratio of the two compounds was determined as 5.4:1.0, or 84% ether to 16% alcohol. In a separate experiment it was shown that the alcohol is stable under the reaction conditions for >10 half-lives.

The isolated products were also analyzed using a Varian HA-100 nmr spectrometer. The doublet due to the methyl resonance adjacent to the methine group in 2-furylmethylcarbinol (δ 1.47 lies slightly downfield from the corresponding doublet in the ether (δ 1.43). Measuring the areas of these superimposed doublets and the triplet for the remaining methyl group, present only in the ether, yields an independent analysis of the product distribution, 13 ± 5% alcohol and 87 ± 5% ether. The HA-100 nmr spectrum of the product mixture showed that no olefin was produced. No vinyl hydrogen resonances, which lie in the δ 5.0–7.0 region in 2-vinylfuran, could be detected. 5-Methyl-2-furylmethylcarbinyl *p*-nitrobenzoate gave a similar product distribution.

Kinetic Procedures.—The kinetic solutions were prepared to be *ca.* 0.013 *M* *p*-nitrobenzoate or chloride in 80% aqueous ethanol. The solvent was prepared by mixing four parts of ethanol with one part of water. The ethanol was purified by distilling commercial absolute ethanol twice from iodine-activated

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magnesium according to the method of Lund and Bjerrum.[35] The water was purified by boiling for several hours and then distilling. The volumes of the purified liquids were measured in pipets and mixed at room temperature. The same pipets were used for the preparation of each bath of solvent.

The kinetic samples were prepared by weighing 0.0013 mol of *p*-nitrobenzoate or chloride into a 100-ml volumetric flask. The flask was filled to the mark with 80% aqueous ethanol and then placed in a constant-temperature bath.

At appropriate time intervals, 5-ml aliquots were withdrawn from the reaction flask with a pipet and quenched in a beaker containing 25 ml of absolute alcohol. The liberated *p*-nitrobenzoic acid was titrated with 0.0075 *M* potassium hydroxide in 95% aqueous ethanol with a Metrohm potentiograph E 336A automatic recording titrator using the first derivative of the titration curve. The solvolyses of the chloride were followed in the same way except that the titration curve itself, not the first derivative, was used.

In the case of 4-carbethoxy-2-furylmethylcarbinyl *p*-nitrobenzoate, the solvolysis rate at 94.50° was measured using the sealed ampoule technique.

The solvolysis of 5-methyl-2-furylmethylcarbinyl *p*-nitrobenzoate was too rapid to be followed by titration. An ultraviolet spectrophotometric procedure was used instead. The ultraviolet spectrum of the ester in 80% aqueous ethanol changed in a first-order manner to that of the reaction products if a slight amount of sodium bicarbonate was present to keep the liberated *p*-nitrobenzoic acid as the anion. A Gilford Model 2000 automatic recording spectrophotometer was used to follow the progress of the reaction. The ultraviolet spectrophotometric procedure was also used to measure the rate constants for 2-furylmethylcarbinyl *p*-nitrobenzoate and 5-bromo-2-furylmethylcarbinyl *p*-nitrobenzoate. Both methods gave the same rate constant.

Kinetic Calculations.—The first-order rate constants were calculated using a nonlinear least squares program, LSKIN 1,[36] on an IBM 7094 computer. Precision was ±2%. The measured rate constants are given in Tables IV and V.

Results and Discussion

2-Furylmethylcarbinyl *p*-nitrobenzoate itself solvolyzes in 80% aqueous ethanol at 45° to give 2-furylmethylcarbinol (15%) and its ethyl ether (Chart I).

TABLE IV

RATE CONSTANTS FOR THE SOLVOLYSES OF 2-FURYLMETHYLCARBINYL *p*-NITROBENZOATES

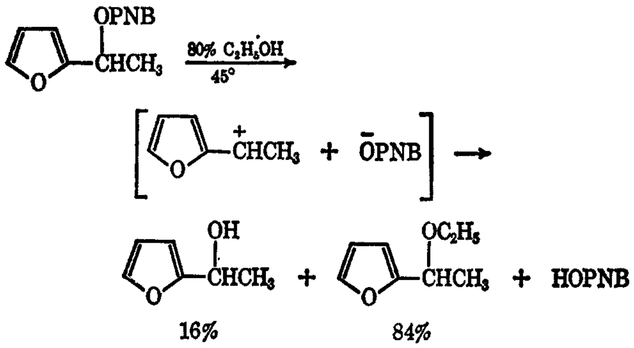
Y	Temp, °C	k_1, sec^{-1}
5-CH$_3$	44.50	1.66×10^{-2} (uv)
	44.50	1.68×10^{-2} (uv)
	25.00	2.50×10^{-3} (uv)
H	44.65	1.33×10^{-4} (uv)
	44.94	1.30×10^{-4}
	44.94	1.29×10^{-4}
	25.00	1.15×10^{-5}
	25.00	1.19×10^{-5}
H, α-D	44.94	1.08×10^{-4}
	44.94	1.09×10^{-4}
5-Br	44.97	3.84×10^{-5}
	44.95	3.85×10^{-5}
	44.65	4.03×10^{-5} (uv)
	25.00	3.17×10^{-6}
4-Br	75.02	2.65×10^{-5}
	44.95	8.21×10^{-7}
4-COOEt	94.50	4.02×10^{-5}
	75.27	5.49×10^{-6}
p-Methoxyphenylmethylcarbinyl *p*-nitrobenzoate	75.02	5.03×10^{-4}
	45.00	2.30×10^{-5}

TABLE V

RATE CONSTANTS FOR THE SOLVOLYSES OF SUBSTITUTED 2-FURYLMETHYLCARBINYL CHLORIDES

Y	Temp, °C	k_1, sec^{-1}
5-COOEt	44.94	1.37×10^{-3}
	44.94	1.34×10^{-3}
	25.02	1.47×10^{-4}
	25.02	1.46×10^{-4}
5-NO$_2$	75.04	9.17×10^{-5}
	44.94	5.22×10^{-6}

CHART I



No 2-vinylfuran is detected. This observation is consistent with the results of Shiner and coworkers,[37] who find that substituted 1-phenylethyl chlorides solvolyze in various aqueous organic solvents to give <1% of olefinic porducts. The solvolysis of 5-methyl-2-furylmethylcarbinyl *p*-nitrobenzoate in 80% aqueous ethanol at 45° gives approximately the same distribution of alcohol and ether. Again no olefin was detected. It is to be noted that we have obtained no evidence indicating the incursion of the abnormal substitution reaction occasionally observed with furfuryl chloride.[38]

The reactivity of 2-furylmethylcarbinyl *p*-nitrobenzoate in 80% aqueous ethanol at 25° is 5.6 times greater than that of *p*-methoxyphenylmethylcarbinyl *p*-nitrobenzoate and $>10^4$ times greater than that estimated for phenylmethylcarbinyl *p*-nitrobenzoate under the same reaction conditions.[39] The very high reactivity of 2-furylmethylcarbinyl *p*-nitrobenzoate is indicative of a limiting solvolysis. However, we sought evidence, other than that derived from ring substituent effects upon reactivity, to demonstrate that the solvolysis of 2-furylmethylcarbinyl *p*-nitrobenzoate was limiting. α-Deuterium isotope effects upon solvolysis rate constants are useful in making this determination.[40–42] Compounds solvolyzing by a limiting mechanism generally are *ca.* 15–20% more reactive than their α-deuterio derivatives. The reactivity of compounds which undergo direct displacement reactions is generally not changed by deuterium substitution at the α position. Recently Jones and Thornton[43] have measured the solvolysis rate constants of methyl chloro-

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[35] H. Lund and J. Bjerrum, *Ber.*, **64**, 210 (1931).

[36] D. F. DeTar and C. E. DeTar, "Computer Programs for Chemistry," D. F. DeTar, Ed., W. A. Benjamin, Inc., New York, N. Y., 1968, Chapter 6. We wish to thank the Computer Center, University of California, for making computer time available to us.

[37] V. J. Shiner, Jr., private communication.

[38] M. E. Runde, E. W. Scott, and J. R. Johnson, *J. Amer. Chem. Soc.*, **52**, 1284 (1930).

[39] S. Winstein and A. H. Fainberg, *ibid.*, **79**, 1597 (1957).

[40] A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *ibid.*, **80**, 2326 (1958).

[41] A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N.Y., 1962, p 173.

[42] V. J. Shiner, Jr., W. E. Buddenbaum, B. L. Murr, and G. Lamatz, *J. Amer. Chem. Soc.*, **90**, 418 (1968).

[43] T. C. Jones and E. R. Thornton, *ibid.*, **89**, 4863 (1967).

TABLE VI

SOLVOLYSIS DATA FOR 2-FURYLMETHYLCARBINYL *p*-NITROBENZOATES IN 80% AQUEOUS ETHANOL AT 25.00°

Compound	k_{rel}	Log k_{rel}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	σ^{+a}
5-CH_3	212	2.33	17.7	−11.0	−0.311
H	1.00	0.00	22.1	−6.9	0.000
5-Br	0.271	−0.57	22.9	−6.7	0.150
5-$CO_2C_2H_5$[b]	3.70×10^{-4} [b]	−3.43	20.4[c]	−7.5[c]	0.482
5-NO_2[b]	1.45×10^{-6} [b]	−5.84	20.3[c]	−19.0[c]	0.790
4-Br	4.76×10^{-3}	−2.32	24.7	−8.6	0.405
4-$CO_2C_2H_5$	7.67×10^{-4}	−3.11	25.6	−9.3	0.366

[a] From ref 45. [b] Extrapolated from the rate data for the chlorides as described in the text. [c] From the chloride.

methyl ether and methyl chloromethyl-d_2 ether in 2-propanol. They found $k_H/k_D = 1.24 \pm 0.08$ per deuterium. Methyl chloromethyl ether has a Grunwald–Winstein *m* value of 1.02 ± 0.03, within experimental error of that (1.00) defined for *t*-butyl chloride, which undergoes a limiting solvolysis.[44] These results establish the applicability of the α-deuterium criterion for systems in which a major share of the positive charge is dispersed to an adjacent oxygen atom (*e.g.*, the 2-furylmethylcarbinyl system).

When 2-furylmethylcarbinyl *p*-nitrobenzoate and its α-deuterio derivative are solvolyzed in 80% aqueous ethanol at 44.94°, the isotope effect is $k_H/k_D = 1.20 \pm 0.01$. This provides strong evidence for a limiting mechanism.

Six ring substituted 2-furylmethylcarbinyl *p*-nitrobenzoates have been prepared (5-CH_3, 5-Br, 5-$CO_2C_2H_5$, 5-NO_2, 4-Br, and 4-$CO_2C_2H_5$). These substituents have widely different effects upon the reactivities of phenyldimethylcarbinyl chloride.[45] Substituents in the furan ring have a dramatic effect upon the reactivity of the furylmethylcarbinyl *p*-nitrobenzoates. Introduction of a 5-methyl group causes a rate acceleration of 212-fold. This is to be contrasted with the 50-fold rate increase observed in the solvolysis of analogous benzyl systems.[46] Conversely, the introduction of a 5-nitro group causes a reduction in reactivity by nearly one million.

Data for the compounds which we have studied are tabulated in Table VI, extrapolated to 25°. In constructing this table, it has been necessary, in addition, to make extrapolations from chloride as the leaving group to *p*-nitrobenzoate (OPNB) as the leaving group for two of the compounds in the series, the 5-carbethoxy substituent and the 5-nitro substituent. Values of the ratio k_{Cl}/k_{OPNB} can be estimated from several sources in the literature. Buckson and Smith[34] have recently measured the solvolysis rate for phenyldimethylcarbinyl *p*-nitrobenzoate, and from these data a value of k_{Cl}/k_{OPNB} of $2.4 \times 10^{+5}$ may be derived using reasonable values in an *mY* correlation.[44] A very similar value ($5.8 \times 10^{+5}$) may be calculated from the data of Goering and his students from the studies of the 5-methyl-2-cyclohexenyl system.[47] Finally extrapolation of our measured rates for *p*-methoxyphenylmethylcarbinyl *p*-nitrobenzoate to 25° in 80% ethanol, and extrapolation of the data of Shiner, *et al.*,[42] on the chloride, gives a value k_{Cl}/k_{OPNB} of 3.37×10^4.

The relative rate sequence in Table VI is constructed using this last and more conservative estimate of the relative reactivity of chlorides and *p*-nitrobenzoates. When the data in Table VI are plotted against σ^+ constants, using σ_p^+ for substituents in the 5 position and σ_m^+ for substituents in the 4 position, a ρ of −7.44 is obtained, correlation coefficient 0.99. This value for ρ is substantially more negative than the ρ of −6 to −6.5 from the data of Shiner, *et al.*,[42] or than the ρ of −6.14 for benzyl tosylates reported by Brown, *et al.*[48]

If one uses the larger value for the rate ratio k_{Cl}/k_{OPNB}, namely 2.4×10^5, the correlation with σ^+ constants is still excellent, and the derived value of ρ is more negative; ρ is −8.25 and the correlation coefficient is 0.986.

Registry No.—4-Carbethoxy-2-acetylfuran, 18753-57-6; α-deuterio-2-furylmethylcarbinyl *p*-nitrobenzoate, 18744-01-9; 5-nitro-2-furylmethylcarbinyl chloride, 18744-02-0; 2-furylmethylcarbinyl ethyl ether, 18744-03-1; 5-carbethoxy-2-furylmethylcarbinyl chloride, 18744-04-2.

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[44] E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, **70**, 846 (1948).

[45] Y. Okamoto and H. C. Brown, *ibid.*, **80**, 4979 (1958).

[46] Many examples could be given. The most recent, and most carefully documented study is undoubtedly that of Shiner, *et al.*[42]

[47] H. L. Goering and E. F. Silversmith, *J. Amer. Chem. Soc.*, **77**, 6249 (1955); H. L. Goering, T. D. Nevitt, and E. F. Silversmith, *ibid.*, **77**, 5026 (1955).

[48] H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Schepple, *ibid.*, **89**, 370 (1967).