hydrochloric acid, and the acidified solution was thoroughly extracted with ether. The combined ether extracts were dried over anhydrous magnesium sulfate and filtered and the solvent was removed by careful distillation. The residue was dissolved in 5 ml of anhydrous ether and this ethereal solution was added slowly to a refluxing solution of 0.075 g of lithium aluminum hydride in 20 ml of ether. After the reaction mixture had been refluxed for 3 hr, the reaction vessel was cooled and 0.300 g of 10% sodium hydroxide solution was added dropwise. The solution was stirred for several hours and the precipitated inorganic salts were removed by filtration. The ether was removed by distillation and the residue was molecularly distilled to give 30 mg of a mixture of alcohols which had infrared and nmr spectra identical with those of the mixture obtained in the third fraction of products isolated from the acid-catalyzed addition of acetic acid to **3**.

Acid-Catalyzed Reaction of 4-Acetoxy-*trans*-bicyclo[5.1.0]octane (24) with Acetic Acid. A sample of **24** was dissolved in acetic acid which was 0.082 *N* in *p*-bromobenzenesulfonic acid. The solution was heated to 80° for 3 hr, cooled, and worked up in a manner similar to that described in the acid-catalyzed addition of acetic acid to **3** (*vide supra*). Vpc analysis showed the presence of a 50% yield of an equimolar mixture of **4** and **5**. In addition the presence of four other components was demonstrated. These components were not present in the reaction mixture obtained from the acid-catalyzed addition of acetic acid to **3**. As a result they were not characterized.

Acknowledgment. We are indebted to the National Science Foundation for a grant which supported this investigation.

Stable Free Radicals. V. The Reaction between 1-Ethyl-4-carbomethoxypyridinyl and Benzyl Halides[1]

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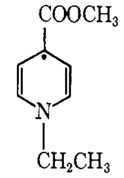
Abstract: The rates of reaction of the stable free radical, Py·, 1-ethyl-4-carbomethoxypyridinyl, with benzyl bromide and a number of benzyl chlorides (4-CH_3O, 4-CH_3, H, 4-Cl, 4-NO_2) have been measured in several solvents and, for the unsubstituted chloride and bromide, at several temperatures. The rate constant for the reaction of Py· with $C_6H_5CH_2Cl$ is little affected by substitution except for the 4-NO_2 derivative, and the solvent effect on the rate is modest for $C_6H_5CH_2Cl$ and $C_6H_5CH_2Br$. Criteria for decisions about the mechanisms of radical reactions are discussed and it is concluded that Py· reacts with benzyl chlorides and bromides (except for the 4-NO_2 compound) in an *atom-transfer* reaction.

Free radicals which are unreactive enough to be transferred and utilized under conditions different from those under which the radical was generated may be termed "stable."[1a,4] Stable radicals offer the opportunity for direct kinetic measurements under different conditions, permitting the use of such mechanistic criteria as solvent sensitivity. In addition, stable radicals discriminate among possible reactants to a far greater extent than reactive radicals and thus offer one of the most sensitive probes into reactivity toward radicals.

We have now examined the rates of reaction of the stable pyridinyl radical, 1-ethyl-4-carbomethoxypyridinyl (**1**), with a number of benzyl halides. The term *atom-transfer reaction* fits the characteristics of most of the reactions examined. One striking exception is the very rapid reaction of **1** with 4-nitrobenzyl halides, which we believe to be an *electron-transfer reaction*. The latter cases are treated in the following article.[5]



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Results

The reaction of pyridinyl radicals with alkyl halides consumes two radicals for each halide (eq 1). The

$$2Py\cdot + RX \longrightarrow Py^+X^- + PyR \qquad (1)$$

ultimate products of the reaction are the pyridinium halide and a mixture of 1,2- and 1,4-dihydropyridines.[1a,c,6]

The rates of reaction are easily measured by following the disappearance of Py· at λ_{max} 6325 (ϵ_{max} 83) or 3950 Å (ϵ_{max} 4700) in the apparatus shown in Figure 1. The rate constants for the reaction of Py· with benzyl halides were calculated from eq 2, corresponding to a mechanism in which a bimolecular reaction between a radical and halide is succeeded by a fast reaction which consumes a second radical (eq 3 and 4).

$$k = \frac{1}{t}\frac{1}{(2A_0 - B_0)} \ln \frac{B_0[(2A_0 - B_0) + B]}{2A_0B} \qquad (2)$$

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[1] Previous articles in this series are: (a) E. M. Kosower and E. J. Poziomek, *J. Amer. Chem. Soc.*, **86**, 5515 (1964); (b) E. M. Kosower and J. L. Cotter, *ibid.*, **86**, 5524 (1964); (c) E. M. Kosower and I. Schwager, *ibid.*, **86**, 5528 (1964); (d) M. Itoh and E. M. Kosower, *ibid.*, **90**, 1843 (1968).

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[4] A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals," Academic Press, New York, N. Y., 1968, p 405.

[5] M. Mohammad and E. M. Kosower, *J. Amer. Chem. Soc.*, **93**, 2713 (1971).

[6] E. M. Kosower and H. P. Waits, Abstracts of the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 109S, and manuscript in preparation.

Table I. Rate Constants for the Reaction of Benzyl Chloride with 1-Ethyl-4-carbomethoxypyridinyl Radical

Halide concn, M^a	Radical concn, M^b	Solvent	Temp,^{c} °C	k_2, M^{-1} sec$^{-1\,d}$
4.0×10^{-2}	4×10^{-4}	CH_3CN	15	$2.6 (\pm 0.6) \times 10^{-4}$
7.45×10^{-2}	3.5×10^{-3}	CH_3CN	20	$1.93 (\pm 0.35) \times 10^{-4}$
0.78	7.8×10^{-3}	CH_3CN	25	$3.31 (\pm 0.3) \times 10^{-4}$
1.40×10^{-2}	3.8×10^{-4}	CH_3CN	35	$6.0 (\pm 0.5) \times 10^{-4}$
3.8×10^{-2}	3.6×10^{-3}	CH_3CN	45	$1.5 (\pm 0.3) \times 10^{-3}$
2.40	0.95×10^{-3}	DME^e	15	$3.6 (\pm 0.6) \times 10^{-6}$
0.82	0.90×10^{-3}	DME	25	$5.3 (\pm 0.7) \times 10^{-6}$
$2.0 (\pm 0.1)$	9.2×10^{-3}	DME	35	$1.40 (\pm 0.25) \times 10^{-5}$
0.67	0.99×10^{-2}	DME	40	$1.45 (\pm 0.15) \times 10^{-5}$
2.67	1.2×10^{-3}	Acetone	25	4.75×10^{-5}

[a] Concentration determined by glc. [b] Concentration determined from optical density measurements at wavelengths described in the text. [c] Thermostat temperature: ±0.3°; reaction vessel maintained at *ca.* ±1°. [d] Rates were measured spectrophotometrically in an all-glass apparatus (see Experimental Section). The rate constants were calculated assuming $A\cdot + BCl \rightarrow ACl + B\cdot$; $B\cdot + A\cdot \rightarrow AB$ (very fast), *i.e.*, the overall reaction is $2A\cdot + BCl \rightarrow$ products, in which A· is the pyridinyl radical; the rate constants are the average of two or more runs. [e] 1,2-Dimethoxyethane.

Table II. Rate Constants for the Reaction of Benzyl Bromide with 1-Ethyl-4-carbomethoxypyridinyl Radical

Halide concn, M^a	Radical concn, M^b	Solvent	Temp,^{c} °C	k_2, M^{-1} sec$^{-1\,d}$
3.0×10^{-3}	2×10^{-4}	DME^e	15	$1.1 (\pm 0.2) \times 10^{-2}$
1.48×10^{-2}	1.27×10^{-2}	DME	20	$9.6 (\pm 1.0) \times 10^{-3}$
2.35×10^{-3}	2.66×10^{-3}	DME	25	$1.50 (\pm 0.3) \times 10^{-2}$
5.65×10^{-3}	4.55×10^{-3}	DME	30	$2.2 (\pm 0.3) \times 10^{-2}$
1.14×10^{-4}	2.90×10^{-4}	DME	35	$4.1 (\pm 0.60) \times 10^{-2}$
2.44×10^{-3}	9.2×10^{-4}	CH_3CN	15	0.15
2.98×10^{-4}	9.2×10^{-5}	CH_3CN	25	0.45

[a] Concentration determined from optical density measurements at 2750 Å and OD *vs.* concentration curve ($\epsilon_{2750} = 4925$). [b] See footnote *b*, Table I. [c] See footnote *c*, Table I. [d] See footnote *d*, Table I. [e] 1,2-Dimethoxyethane.

where A = (RX) and B = (Py·).

$$\mathrm{Py\cdot + RX \longrightarrow PyX + R\cdot} \tag{3}$$

$$\mathrm{Py\cdot + R\cdot \longrightarrow PyR} \tag{4}$$

Rate constants for the reaction of benzyl chloride with pyridinyl radical **1** in acetonitrile, 1,2-dimethoxyethane, and acetone are listed in Table I and activation parameters in Table III.

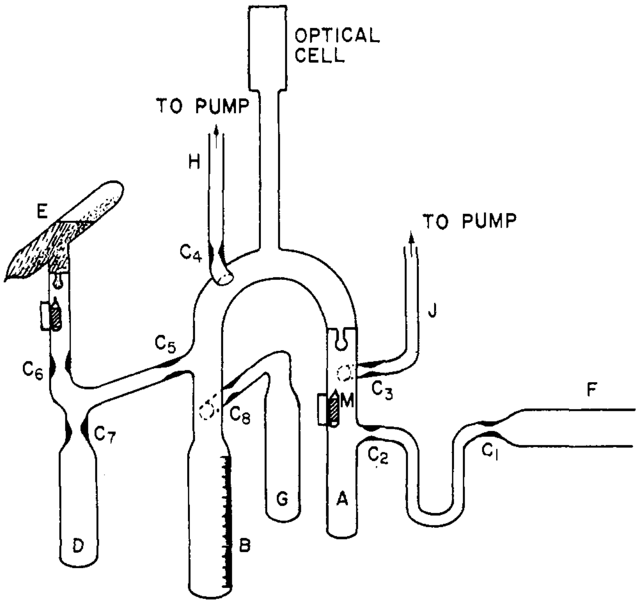

Figure 1. Apparatus for the study of the reaction of low concentrations of 1-ethyl-4-carbomethoxypyridinyl radical with substituted benzyl chlorides.

Benzyl bromide reacts with **1** about 1000 times faster than does benzyl chloride. Rate constants are listed in Table II, and the activation parameters are shown in Table III.

Substituted benzyl chlorides react with **1** at rates which do not differ very much from those found for the unsubstituted chloride, except for the 4-nitrobenzyl chloride.[5] The rate constants for the reaction of radical **1** with 4-methoxy-, 4-methyl-, 4-chloro-, and 4-nitrobenzyl chlorides in acetonitrile are listed in Table IV.

The effect, large or small, of solvent change on some of the reactions of pyridinyl radical **1** with halides is illustrated in Table V.

Discussion

To provide an appropriate context for our discussion, criteria are set forth for decisions about radical reactions. The most important elementary reactions of radicals are combination, atom transfer, addition, and electron transfer.

Criteria for Mechanisms. All of the pyridinyl radical reactions with halides thus far investigated are bimolecular, so that unimolecular reactions (*i.e.*, formation of a highly reactive isomeric radical in a rate-limiting step) do not have to be considered for the present. Most other criteria for mechanisms depend upon perturbation of the reaction system, and these may be conveniently divided into intramolecular and extramolecular. Illustrations of the perturbation of a reaction system (original, eq 5) are given in eq 6 (major or structural, minor or substituent change in A) and eq 7

$$\mathrm{R\cdot + AX \longrightarrow} \text{ original system, reference reaction} \tag{5}$$

$$\mathrm{R\cdot + A'X \longrightarrow} \text{ perturbed system, major or minor change in A} \tag{6}$$

$$\mathrm{R\cdot + AX' \longrightarrow} \text{ perturbed system, change in X} \tag{7}$$

(change in "leaving group"). A change in the reaction

Table III. Activation Parameters for the Reaction of Benzyl Chloride and Benzyl Bromide with 1-Ethyl-4-carbomethoxypyridinyl[a]

Benzyl halide	Solvent	E_a*, kcal/mol	$\Delta H_{25°}$*, kcal/mol	$\Delta S_{25°}$*, eu	$\Delta F_{25°}$*, kcal/mol
Chloride	CH_3CN	12.2	11.6	−36	22.2
	DME[b]	12.6	12.0	−42	24.7
Bromide	CH_3CN				17.9
	DME[b]	11.8	11.2	−29.4	19.9

[a] Based on data in Tables I and II. [b] 1,2-Dimethoxyethane.

Table IV. Rate Constants for the Reaction of 4-Substituted Benzyl Chlorides with Pyridinyl Radical in Acetonitrile at 25°

4-Substituent, benzyl chloride[a]	Halide concn, M[b]	Radical, concn, M[c]	k_2, M^{-1} sec^{-1} [d]
4-CH_3O	0.45	1.63×10^{-2}	11.3×10^{-4}
4-CH_3	0.55	2.26×10^{-2}	3.68×10^{-4}
4-H	0.78	7.8×10^{-3}	3.31×10^{-4}
4-Cl	0.45[e]	1.0×10^{-2}	6.5×10^{-4}
4-NO_2	5.4×10^{-6} [e]	1.02×10^{-5}	$240{,}000{,}000 \times 10^{-4}$ [f]

[a] Benzyl halides were purified as described in the text. [b] Concentrations determined by glc except as noted. [c] Concentrations determined from optical density measurements as described in the text. [d] Second-order constants (except for 4-NO_2 derivative) were derived from measured pseudo-first-order constants by dividing by the halide concentration and by a factor of 2, the number of radicals disappearing in each reaction. [e] Concentrations determined from the optical density at 2250 Å (ε 12,080) (4-Cl) and 2650 Å (ε 10,500) (4-NO_2). [f] Second-order rate constants determined by the techniques described in the following article.

Table V. Solvent Effect on the Rate Constants for the Reaction of Halides with 1-Ethyl-4-carbomethoxypyridinyl Radical at 25°

Halide	Solvent	Z value, kcal/mol[a]	k_2, M^{-1} sec^{-1}	k_{rel}[f]
Benzyl chloride[b]	DME[c]	59.2	5.3×10^{-6}	
	Acetone	65.7	47.5×10^{-6}	
	CH_3CN	71.3	331×10^{-6}	63
Benzyl bromide[d]	DME[c]	59.2	1.50×10^{-2}	
	CH_3CN	71.3	45×10^{-2}	30
4-Nitrobenzyl chloride[e]	DME[c]	59.2	8.3	
	CH_3CN	71.3	24,000	2900
Dibromomethane[g]	CH_2Cl_2	64.2	0.48	~0.5[i]
	$(CH_3)_2CHOH$	75.8[h]	0.28	

[a] Z values (*cf.* E. M. Kosower, "Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968) were checked at infinite dilution (*cf.* following paper). [b] See Table I. [c] 1,2-Dimethoxyethane. [d] See Table II. [e] See following paper. [f] Rate constant for reaction of pyridinyl radical **1** in acetonitrile divided by that for the reaction in 1,2-dimethoxyethane. [g] Reference 1c. [h] Measured value in the presence of 1 M dibromomethane. [i] Note that Z value change is close to that used in other cases.

Table VI. Magnitudes of Effects Expected upon Perturbation of Elementary Reaction Systems

	Intramolecular perturbations		Extramolecular perturbations	
Elementary reactions	Structural (major change in A)	Substituent (minor change in A)	Element (change in X)	Solvent polarity
Atom transfer	Large	Modest	Large	Modest
Combination	Modest	Small		Small
Addition	Large[a]	Small[b]	Small	Small
Electron transfer	Large	Large	Large	Large

[a] *Cf.* W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1962, Table 14-9, p 225. [b] See footnote *a*, Tables 16-1 and 16-3, pp 255 and 262.

medium (*i.e.*, a solvent change) is an extramolecular perturbation of the original system. The original reaction system thus serves as the reference with which the effects of the perturbations may be measured.

The effects produced by the perturbations can be predicted (Table VI). Let us consider the application of these criteria to the problem of the mechanism of the reaction between pyridinyl radical and benzyl halides.

Element Effect. Replacement of chlorine by bromine in benzyl halides leads to a rate of reaction about 10^3 greater with pyridinyl radical **1**. A similar ratio obtains for the rate constants for the reaction of pyridinyl radical **1** with bromochloromethane and dichloromethane. The *element effect* for the reaction of **1** with alkyl halides is large. We may thus exclude addition as an elementary step in the rate-limiting phase of the reaction.

Substituent Effect. Variation of the 4 substituent of the benzyl chloride has relatively little effect on the rate of the reaction with pyridinyl radical **1**, a 4-methoxybenzyl chloride reacting only 3.4 times as fast as benzyl chloride, and the ρ value less than ±2. The maximum possible substituent effect on a reaction should be observed if that reaction involves the loss or gain of an electron. In the present instance, an appropriate reference reaction for the evaluation of substituent effects is the one-electron reduction of benzyl chlorides.[7]

$$C_6H_5CH_2Cl + e^- \rightleftharpoons C_6H_5CH_2Cl\cdot^- \quad (8)$$

The one-electron reduction potentials for benzyl chloride and 4-nitrobenzyl chloride are, respectively, −2.20 and −1.16 V *vs.* silver–silver perchlorate in acetonitrile.[5] A ρ value may be derived from these data by converting the voltage difference into kilocalories per mole by dividing by 2.3*RT* and the difference

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(7) Previous literature is summarized in J. G. Lawless, D. E. Bartak, and M. D. Hawley, *J. Amer. Chem. Soc.*, **91**, 7121 (1969).

Table VII. Pyridinyl Radical-Halide Reactions. Solvent Effect on Transition State Free Energies[a]

Halide reactant	$\Delta\Delta F^*$, kcal/mol	$0.5\Delta Z$, kcal/mol	$\Delta\Delta F^*/0.5\Delta Z$
Benzyl chloride	2.45	6.05	0.405
Benzyl bromide	2.01	6.05	0.333
4-Nitrobenzyl chloride	4.72	6.05	0.781
Dibromomethane	−0.319	5.80	−0.055

[a] Rate data and solvent polarity values are recorded in Table V. All calculations are for 25°.

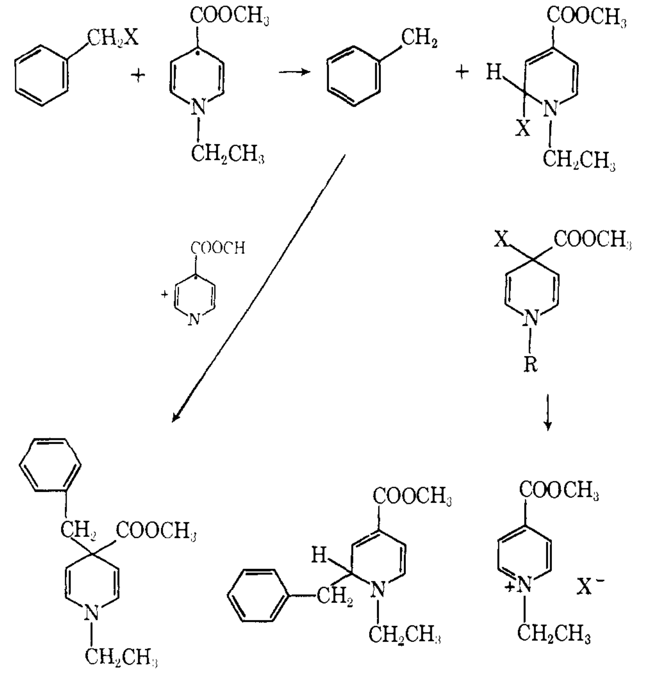
in σ_p constants between 4-H and 4-NO_2 or 1.24.[8] The ρ value thus found is +14, a number quite close to the ρ value for the electron transfer indicated by the charge-transfer absorption of pyridinium iodides.

The ρ values presented here suggest that a choice between electron transfer and some other kind of elementary reaction may be made on the basis of the ρ value. The ρ value for the reaction of substituted benzyl chlorides with pyridinyl radical (with the exception of 4-nitrobenzyl chloride) is far too low for the reaction to be an electron-transfer reaction.

Solvent Effect. The solvent effect on the reactions of benzyl chloride and bromide with pyridinyl radical **1** is modest. A comparison of $\Delta\Delta F^*$, the change in transition state free energy divided by one-half the change in Z value, provides a convenient index of the responsiveness of a reaction system to medium change. A listing of the values we have obtained for the quantity $\Delta\Delta F^*/0.5\Delta Z$ is given in Table VII.

The scale of solvent sensitivities defined in terms of $\Delta\Delta F^*/0.5\Delta Z$ runs from *ca.* 0 to *ca.* 1. The relative rates observed for such solvent sensitivities indicate the difference between reaction classes much more strikingly, as the values for k_{rel} in Table V show. From the list in Table VI, we may conclude that atom transfer is the rate-limiting step in the reaction of pyridinyl radical with most of the benzyl halides.

Scheme I



Mechanism of the Reaction of Pyridinyl Radical with Benzyl Chloride and Bromide. On the basis of bimolecular kinetics, the element effect, the substituent effect, and the solvent effect, atom-transfer is clearly the best choice for the rate-limiting elementary step in the reaction of benzyl chloride and bromide with pyridinyl radical **1**. The overall mechanism is shown in Scheme I. The halogen atom is transferred to the pyridinyl radical, producing a halodihydropyridine and a benzyl radical. The latter rapidly reacts with a second pyridinyl radical to yield a mixture of isomeric dihydropyridines. The halodihydropyridine dissociates to produce a pyridinium halide.

Experimental Section

Materials. **Benzyl chloride,** Eastman Kodak White Label, was dried over magnesium sulfate and distilled *in vacuo*. The middle fraction was degassed by several freeze-thaw cycles and then fractionated in an "isolated" fractionating column (which had been evacuated and sealed off at ~10^{-6} mm) over a water bath. The middle fraction was retained. The final samples were vacuum distilled from this sample again, retaining the middle fraction. Purity of the sample used was over 99.9% (no other peaks visible on glc). Identity was confirmed with nmr.

4-Methylbenzyl chloride, Aldrich Chemical Co., was purified as recommended by Perrin.[10] The middle fraction was then subjected to the same purification procedure (and purity test) adopted for benzyl chloride.

4-Methoxybenzyl chloride (anisyl chloride) was prepared by mixing anisyl alcohol (Eastman Kodak White Label) and thionyl chloride (Matheson Coleman and Bell, sample redistilled). Excess thionyl chloride was distilled off under reduced pressure and the anisyl chloride was fractionated under vacuum and the middle fraction collected. The product gave nmr in agreement with the structure. Final purification was effected by redistilling the above sample at 10^{-6} mm and room temperature by intermittent cooling of the receiver with liquid nitrogen; the middle fraction was collected.

4-Chlorobenzyl chloride, practical grade (Eastman Kodak), was dissolved in a mixture of anhydrous ether and heptane, and dried over calcium sulfate (anhydrous). Ether was removed at reduced pressure and the chloride crystallized from the *n*-heptane at 0° while on the vacuum line. The *n*-heptane was filtered off, the solvent distilled back, and the cold suspension once again filtered. The chloride was further purified by partial freezing, washing the solid with its own melt, and filtering. Finally, the chloride was vacuum distilled.

4-Nitrobenzyl chloride (Eastman Kodak) was twice crystallized from carbon tetrachloride (Perrin[10]), then vacuum sublimed. The purity was checked with thin layer chromatography and was at least 99.5%. The vacuum sublimed sample was kept in the dark and over Drierite ($CaSO_4$). The samples were resublimed under vacuum before use in kinetics.

Benzyl bromide (K & K Laboratories) was purified according to Perrin,[10] then thoroughly degassed at 10^{-6} mm and redistilled (distillation and other manipulations were carried out without exposing the bromide to light). The fraction gave the reported uv spectrum (λ_{max} 2267 Å, ϵ_{max} 8200 in CH_3CN).

Solvents. Acetonitrile, methylene chloride, acetone, and 2-propanol (all spectrograde) were degassed by numerous freeze-thaw cycles and distilled onto degassed molecular sieve (Linde 4-A, heated to 450° in a quartz flask with ₸ 19/38 joint, for several hours while pumping). 1,2-Dimethoxyethane (Eastman Kodak) was vacuum distilled from lithium aluminum hydride. The middle fraction was distilled onto potassium mirror or sodium-potassium alloy.

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(8) Usual practice in organic polarography has been to report the Hammett correlations in volts.[9] Comparison to other organic reactions is facilitated by making the conversion to the usual Hammett ρ value. At 25°, multiplication by 17 converts the value in volts to the usual value.

(9) See, for example, P. Zuman, *Progr. Phys. Org. Chem.*, 5, 164 (1967).

(10) D. D. Perrin, W. L. F. Amargo, and D. R. Perrin, "Purification of Laboratory Chemicals," Pergamon Press, Oxford, 1966, p 362.

1-Ethyl-4-carbomethoxypyridinyl radical (Py·) was prepared as described previously.[1a,6] Solutions of the radical in acetonitrile were stored in break-seal tubes in the freezer. Solutions of the radical in other solvents were prepared by removal of the acetonitrile and addition of purified, degassed solvent.

Rate Measurements. The apparatus used for studies of the reaction of 4-substituted benzyl chlorides with Py· (at concentrations greater than 10^{-3} M) was similar to that previously used[1c] except that all-glass connections replaced the stopcock. For reactions with concentrations of radical below 10^{-3} M, the apparatus shown in Figure 1 was used. After cleaning and flaming, a weighed amount of 4-nitrobenzyl chloride in a glass ampoule was put into F, the end sealed off, and the halide sublimed into the U tube after evacuation through J. After sealing at C_1, then C_3, the halide was sublimed into A and C_2 sealed off.

The apparatus, with the free radical ampoule (as shown in Figure 1) was connected to the pump through H and baked under vacuum. The free radical solution was allowed to run into D and after sealing C_6 and then C_4, the reaction vessel was rinsed with free radical solution and then rinsed with the solvent distilled from the free radical. A dilute solution ($\sim10^{-5}$ M) of free radical is obtained by distillation from D to B. After having the desired volume of the solution, D was sealed off at C_5. (In some cases, D was another break-seal ampoule to retain the unused portion of the free radical.) Preliminary optical spectra were taken to find the concentration ($\sim10^{-5}$ M) and the purity of the free radical solution. The side-arm tube G was then used to bring the concentration of the free radical in the desired range.

Before reaction, free radical stability was checked for 30–120 min; if any absorption changes were noted, the sample was rejected. The break-seal of the tube A was broken and the solution shaken without mixing, then checked for 15–30 min to ensure the absence of leaks in A.

The reactants were then mixed and the decrease in optical density with time was followed by scanning the near-ultraviolet and ultraviolet spectrum of the free radical. Reactions were followed at 3950 or at 6300 Å, either with scans or at a single wavelength.

Another optical cell was attached to the compartment A for CH_3CN and DMF to facilitate the start of recording.

Rate measurements at elevated temperature were generally carried out in a sealed Pyrex square cell to prevent distillation of the solvent.

The concentrations of the halides were determined by glc or titration. The concentration of 4-nitrobenzyl chloride was determined from the weight of the amount introduced and from the total volume of the solution. Quantitative sublimation was checked spectroscopically. The concentration of benzyl bromide was determined spectroscopically from standards at 2750 Å or at λ_{max} 2267 Å (ϵ 8200).

The extinction coefficients of the free radical in the near-uv region in the solvents acetonitrile and DME were determined by titration against methyl viologen dichloride and measurement of the concentration of methyl viologen cation radical (λ_{max} 6050, ϵ_{max} 10,060).[1b]

Acknowledgment. Grateful acknowledgment is made for support from the National Institutes of Health, the Army Research Office (Durham), the Petroleum Research Fund (PRF-3695A1), Edgewood Arsenal, and the National Science Foundation.

Stable Free Radicals. VI. The Reaction between 1-Ethyl-4-carbomethoxypyridinyl Radical and 4-Nitrobenzyl Halides[1]

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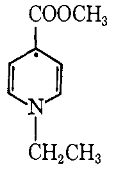
Received July 6, 1970

Abstract: Reaction rates for the stable free radical, 1-ethyl-4-carbomethoxypyridinyl (Py·) (**1**), with 4-nitrobenzyl fluoride, chloride, and bromide are extremely sensitive to solvent polarity (criterion: Z values). The constant for the chloride increases from 1.62 M^{-1} sec^{-1} in 2-MTHF (E_a = 6 kcal/mol) to 24,000 M^{-1} sec^{-1} in CH_3CN, results compatible only with an electron-transfer mechanism. Polarographic reduction potentials are reported for benzyl chloride (−2.20 V), benzyl bromide (−1.67 V), 4-nitrotoluene (−1.505 V), 4-nitrobenzyl fluoride (−1.40 V), 4-nitrobenzyl chloride (−1.16 V), and 4-nitrobenzyl bromide (−0.95 V) [reference $Ag^0/AgClO_4$ in CH_3CN]. Use of the rate and polarographic data along with some information on nitrobenzyl halide radical anion intermediates leads to a four-step mechanism for the reactions of Py· with 4-nitrobenzyl halides: (1) relatively fast electron transfer, (2) dissociation of the initial pyridinium 4-nitrobenzyl halide radical anion pair, (3) decomposition of the 4-nitrobenzyl halide radical anion to halide ion and 4-nitrobenzyl radical, and (4) rapid reaction of Py· and 4-nitrobenzyl radical. Our analysis suggests that the rate-limiting steps in CH_3CN are not the same for the three halides: bromide, step 1; chloride, step 2; and fluoride, step 3.

The stable pyridinyl radical, 1-ethyl-4-carbomethoxypyridinyl (**1**), reacts with 4-nitrobenzyl chloride far more rapidly than might have been anticipated on the basis of the rate constants found for a number of substituted benzyl chlorides.[4] The anomalous rate



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indicated that the mechanism of the reaction was different from the atom-transfer process found for the other benzyl chlorides. The nature of 4-nitrobenzyl

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(1) The previous article in this series is M. Mohammad and E. M. Kosower, *J. Amer. Chem. Soc.*, **93**, 2709 (1971).

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(4) A preliminary report has been published: E. M. Kosower and M. Mohammad, *J. Amer. Chem. Soc.*, **90**, 3271 (1968).