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Stable Free Radicals. 7. 1-Alkyl-4-carbomethoxypyridinyls

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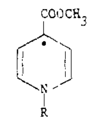
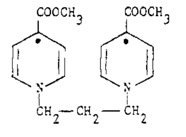
The synthesis of the 1-*tert*-butyl-4-carbomethoxypyridinyl radical is described and its properties are compared with the corresponding 1-methyl, 1-ethyl, and 1-isopropyl radicals. Although the *tert*-butyl radical appears to be the most stable in pure form and less susceptible to π-mer formation, its chemical reactivity toward bromochloromethane is very similar to that of the other 1-alkyl radicals. The nature of the products of reaction of 1-isopropyl-4-carbomethoxypyridinyl with bromochloromethane has been elucidated.

Stable pyridinyl radicals[2,4] (1) were first isolated in 1963[5] and have since proven useful for mechanistic studies.[6,7] Pyridinyl diradicals (e.g., 2) were also prepared and examined.[8,9]



1

R = CH_3, CH_3CH_2, $(CH_3)_2CH$, $(CH_3)_3C$



2

The formation of π-mers from pyridinyl monoradicals (intermolecular)[10] and from diradicals[9,11] (intramolecular) made necessary an understanding of the effect of *N*-alkyl substitution on the properties of pyridinyl monoradicals. Our more recent discovery of pyridinyl radical complexation with bis(pyridinium) ions[12] accentuated the need. Although the 1-ethyl radical has been described previously,[13] only few data have been noted for the 1-methyl and 1-isopropyl radicals.[10] We have now been able to complete the series with the 1-*tert*-butyl radical and shall describe in this article the preparation and certain properties of the simplest 1-alkyl-4-carbomethoxypyridinyl radicals (1).

Results

Synthesis of Salts. Methyl isonicotinate readily reacts with methyl, ethyl, and isopropyl iodides to form the desired salts

Table I. Visible Absorption Maxima for 1-Alkyl-4-carbomethoxypyridinyls in Acetonitrile and 2-Methyltetrahydrofuran

Radical	Registry no.	Solvent, λ_{max} (nm)	
		CH_3CN	2-MF[a]
CH_3	64754-20-7	635	647.5
CH_3CH_2	39327-12-3	632.5	642.5
$(CH_3)_2CH$	64754-19-4	630	637.5
$(CH_3)_3C$	64754-21-8	618	627.5

[a] 2-Methyltetrahydrofuran

(eq 1). *tert*-Butyl iodide could not be induced to react in this way, nor did the usual Zincke reaction via the inaccessible 1-(2,4-dinitrophenyl)-4-carbomethoxypyridinium chloride succeed. An important improvement introduced by Verhoeven[14] permitted us to prepare the *p*-toluenesulfonate salt, and from that the 1-*tert*-butyl-4-carbomethoxypyridinium iodide could be prepared (eq 2). The *tert*-butyl salt was not especially unstable, had a yellow color, and exhibited charge-transfer bands at slightly longer wavelengths than the 1-ethyl salt.

$$\underset{\text{methyl isonicotinate}}{RI + NC_5H_4COOCH_3} \rightarrow \underset{3}{RNC_5H_4COOCH_3^+I^-} \quad (1)$$

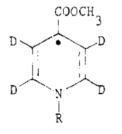
$$R = CH_3, CH_3CH_2, (CH_3)_2CH$$

$$1\text{-}[2,4\text{-}(NO_2)_2C_6H_3]NC_5H_4COOCH_3^+\ OTs^- + t\text{-}BuNH_2 \rightarrow \xrightarrow{NaI} 3 \quad (2)$$

$$R = (CH_3)_3C$$

Methyl isonicotinate-d_4 (88 ± 2% deuterated by NMR) was prepared from 4-picoline-d_4 through oxidation with hot aqueous $KMnO_4$. The deuterated picoline was prepared through Pd-C catalyzed exchange at 240 °C on 4-picoline using D_2 and D_2O.[15,16] 1-Methyl-4-carbomethoxypyridinium-d_4 and -d_7 iodides were prepared through reaction of the ester with CH_3I and CD_3I, respectively.

Preparation of Radicals. All four 1-alkyl-4-carbomethoxypyridinyls and the deuterated radicals **4a** and **4b** were prepared through sodium amalgam reduction of the corresponding salt in acetonitrile under oxvgen-free conditions (eq 3) (1-ethyl and 1-isopropyl radicals[17]). Reduction of the 1-methyl salt was carried out between −30 and −40 °C; the more reactive 1-methyl radical still contained other light-absorbing impurities even after two distillations. Successive extractions (benzene, isopentane) were utilized for the 1-*tert*-butyl radical to avoid a volatile impurity (probably *tert*-butyl iodide).



4a R = CH_3; **4b** R = CD_3

$$\underset{3}{RPy^+I^-} \xrightarrow[CH_3CN]{3\%\ Na(Hg)} \underset{1}{RPy\cdot} \quad (3)$$

Physical Properties of Radicals: (a) Volatility and Appearance. Distillation of the radicals suggests the following order of volatility: isopropyl > ethyl > *tert*-butyl ≃ methyl. The isopropyl radical forms long blue needles at room temperature (mp ~50 °C) and small blue needles mp >25 °C of the *tert*-butyl radical can be obtained on crystallization from isopentane. Both ethyl[13] and methyl radicals are deep emerald-green liquids at room temperature, but both yield sapphire-blue solids at low temperatures.

(b) Visible Absorption Spectra. The maximum of the weak absorption band of the spectra of 1-alkyl-4-carbomethoxypyridinyls shifts to shorter wavelengths as the branching of the 1-alkyl group increases, the effect being slightly more evident in a less polar solvent (Table I). [In the UV, the 392-nm peak for the 1-*tert*-butyl radical was about 15% more intense (ϵ_{max} 5450) than that for the 1-ethyl radical (ϵ_{max} 4700).] The absorption coefficient for the visible band increased substantially (up to twofold) for the ethyl and isopropyl radicals, modestly for the methyl radical (due to accompanying decomposition), and not at all for the *tert*-butyl radical at room temperature in concentrated solutions (2 M for all radicals except *tert*-butyl, for which 0.2 M was the concentration used).

A dilute solution of *tert*-butyl radical (1.5 × 10^{-3} M) in MTHF showed no increase in light absorption between 500 and 1000 nm on cooling to −118 °C, but a more concentrated solution (0.05 M) exhibited a weak absorption at 650 ± 10 nm at the low temperature. *tert*-Butyl π-mer, observed at low temperatures, has λ_{max} 660 (ϵ >100).[18a]

(c) Photoelectron Spectrum. Ionization Potential. Using a moderately concentrated solution of 1-ethyl-4-carbomethoxypyridinyl radical sent by air from Tel-Aviv to Sussex, Murrell and Suffolk[18b] reported an adiabatic ionization potential of 6.8 eV and a vertical ionization potential of 7.2 eV for the radical.

(d) EPR Data. EPR spectra for the 1-alkyl-4-carbomethoxypyridinyls in 2-methyltetrahydrofuran (MTHF) are illustrated in Figure 1: 1-methyl (36.8 G), 1-ethyl (27.4 G), isopropyl (20.8 G), *tert*-butyl (20.8 G). Hyperfine splitting constants, $a_N \simeq$ 6.3–7.0 G and 2,6 $a_H \simeq$ 3.4 G, accounted for the main features of the spectra with complexities introduced by two different orientations of the carbomethoxy group.

Cooling concentrated (0.05 M) MTHF solutions of 1-methyl, 1-ethyl, or 1-isopropyl radicals to 77 K caused a substantial loss in signal strength, as expected for the formation of diamagnetic dimers.[10] In each case, a triplet signal (ca. 0.1–0.2% of radical in this form) was noted with a full-field separation of 83 G for the 1-ethyl case. A half-field signal comparable in strength to that of the full field was observed. The results for the 1-ethyl radical have been confirmed by Ikegami, Watanabe, and Seto,[19] who also noted a concentration dependence for the signal.

A solution of the 1-*tert*-butyl radical (0.05 M in MTHF) exhibited a substantial decrease in signal strength (67%) on cooling from 25 °C to 187 K.

Further cooling to 103 K led to an increased signal strength (two times that at 19 °C) with no sign of triplet signal.

Chemical Properties of Radicals. (a) Thermal Stability. Obvious differences in the stability of the pure radicals appeared during their preparation, with the methyl radical clearly susceptible to decomposition as seen through the loss of volatile material. Using a very short-path-length cell (0.005 cm) it was possible to follow the loss of visible absorption for 2 M acetonitrile solutions of the radicals. Decomposition did not follow simple kinetic laws (first or second order). No decomposition was observed for the *tert*-butyl radical. Approximate half-lives for the decomposition reaction of each radical can be stated: methyl (1 h), ethyl (13 h), isopropyl (≫100 h), *tert*-butyl (≫140 h), all values applying to 2 M solution. In the course of other experiments, we have heated 10^{-3} M solutions of the 1-ethyl radical in acetonitrile for several days at 71 °C with only a 3–4% decrease in optical density in the visible region.

(b) Reaction with Bromochloromethane: Kinetics. The rate of reaction of the alkylpyridinyls with bromochloromethane was followed at 25 °C in acetonitrile solution using the 620–640-nm visible absorption band of the radicals. The reaction has been shown to proceed according to the atom-

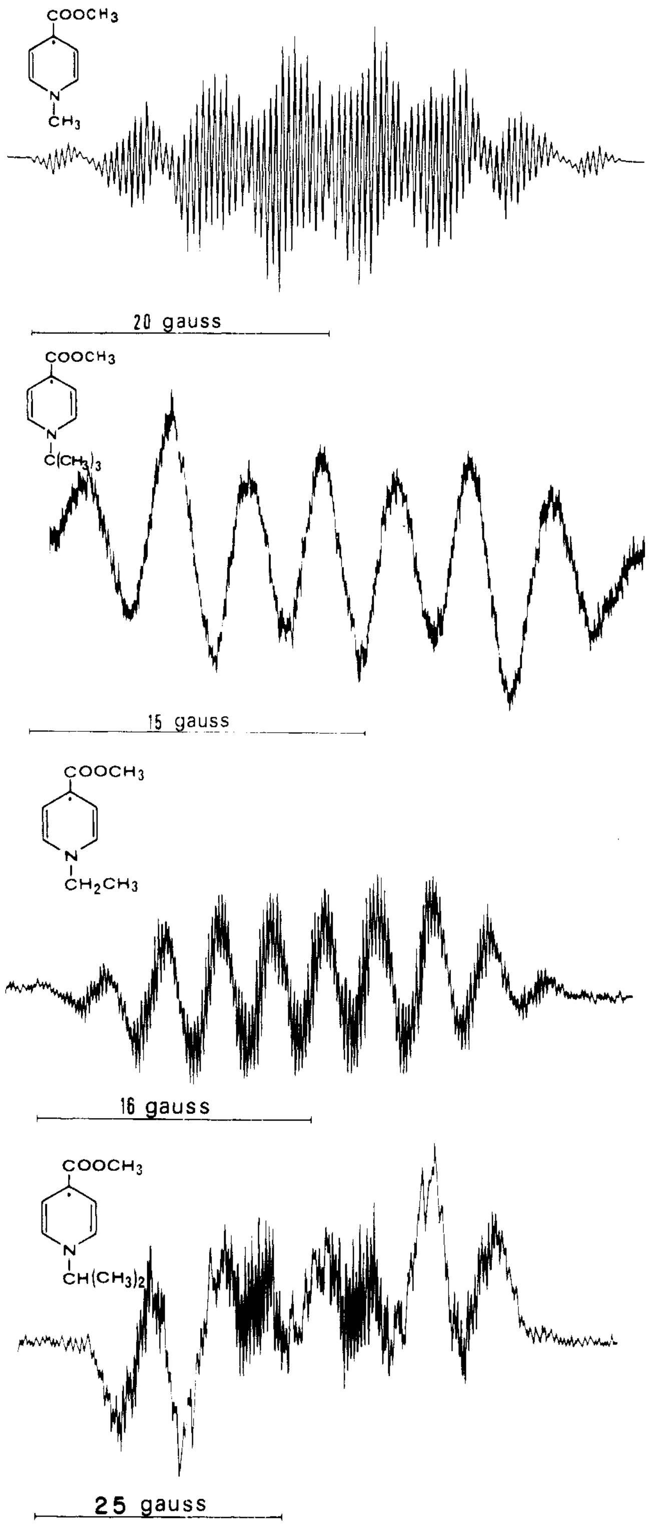


Figure 1. EPR spectra of 1-alkyl-4-carbomethoxypyridinyls in 2-methyltetrahydrofuran.

transfer pathway outlined in eq 4–6.[6,20] The kinetic constants are summarized in Table II.

$$\mathrm{RPy\cdot + BrCH_2Cl \rightarrow RPyBr + \cdot CH_2Cl} \quad (4)$$

$$\mathrm{RPy\cdot + \cdot CH_2Cl \rightarrow RPyCH_2Cl} \quad (5)$$

$$\mathrm{RPybr \rightarrow RPy^+Br^-} \quad (6)$$

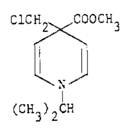
Table II. Rates of Reaction of Alkylpyridinyls with Bromochloromethane in Acetonitrile at 25 °C

1-Alkyl group	$[BrCH_2Cl]$, M	$k_{obsd} \times 10^4$, s^{-1}	$k_2 \times 10^5$,[a] M^{-1}, s^{-1}
Me	1.10	1.05	4.79
	1.13	1.17	5.21
	1.15	1.20	5.21
			(av 5.07)
Et	0.859	0.861	5.02
	1.45	1.46	5.05
	1.54	1.40	4.54
			(av 4.87)
i-Pr	1.10	1.42	6.45
	1.14	1.37	6.01
	1.36	1.62	5.97
			(av 6.14)
t-Bu	1.66	2.29	6.90
	2.42	3.93	8.12
			(av 7.51)

[a] The rate constant, k_2, was corrected by dividing by the number of pyridinyl radicals consumed (two) for every molecule of reacting halocarbon.

(c) Reaction with Bromochloromethane: Products. The reaction of a large quantity of 1-isopropyl-4-carbomethoxypyridinyl with bromochloromethane in acetonitrile was carried out for the purpose of determining the products of the reaction. The 1-isopropyl-4-carbomethoxypyridinium bromide salt (see eq 6) was isolated in over 35% yield and identified by UV, IR, and NMR spectra. We have shown elsewhere that eq 4 is required by the solvent effect data, there being almost no effect of solvent polarity on the rate of the closely related reaction of the 1-ethyl radical with dibromomethane.[6] In other words, the unstable bromodihydropyridine is an intermediate in the reaction, although not detected directly in this case. It is worth noting that 1-methyl-3,5-dicyano-4-iodo-1,4-dihydropyridine dissociates with difficulty even in aqueous solution.[21]

The other product was identified as a mixture of dihydropyridines 4 and 5. These compounds were sensitive to oxygen and were thermally unstable,[22] making detailed characterization very difficult. Similar compounds have been shown to rearrange by Eisner and co-workers.[23] Identification was aided greatly by the presence of the isopropyl group, since two sets of characteristic doublets appeared in the NMR spectrum of the mixture at δ 1.25 and 1.30. The roughly equal peak heights indicated that 1-isopropyl-4-carbomethoxy-4-chloromethyl-1,4-dihydropyridine (4) and 1-isopropyl-2-chloromethyl-4-carbomethoxy-1,2-dihydropyridine (5) were formed in roughly equal amounts. Strong peaks centered at δ 3.7 and 3.8 indicated the methyl groups of the ester and small peaks at δ 4.5 and 6.1 were those expected for dihydropyridines.[22]



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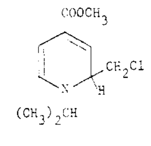

5

Discussion

The survey we have carried out on some of the physical and chemical properties of the 1-alkyl-4-carbomethoxypyridinyls has revealed that several are dependent upon the nature (and size) of the 1-alkyl group.

EPR Spectra. The width of the EPR spectrum for a 1-alkyl-4-carbomethoxypyridinyl is very much dependent upon the number of hydrogens on the α-carbon of the alkyl group. The spectral widths for the spectra shown in Figure 1 are:

Table III. Coupling Constants for Deuteropyridinyl Radicals

Solvent	a_N (**4b**), G	$a_{H(CH_3)}$ (**4a**), G	Spectral width (**4a**),[a] G
Water–acetonitrile (1:9)	6.35 ± 0.05	5.50 ± 0.08	29.19 ± 0.03
Methanol–acetonitrile (1:9)	6.36 ± 0.02	5.45 ± 0.04	29.07 ± 0.02
Acetonitrile	6.37 ± 0.07	5.87 ± 0.08	30.34 ± 0.02
Benzene	6.50 ± 0.04	5.94 ± 0.06	30.81 ± 0.02

[a] Total width (i.e., total splitting) of the spectrum in gauss was measured between points of zero slope on the first derivative spectrum.

(1-alkyl group) CH_3, 36.8 G; CH_3CH_2, 27.4 G; *i*-Pr, 20.8 G; and *t*-Bu, 20.8 G. In addition, as illustrated in Figure 2, the spectral width for the CH_3-d_4 radical is 29.2 G and that for CD_3-d_4 is 12.7 G. The nitrogen splitting appears to increase slightly from the 1-CH_3 (6.26 G)[10] to the 1-$(CH_3)_3C$ ($\simeq$7.0 G). Solvent polarity (*Z* value range[24,25] ~20) change has only a minor effect on the nitrogen splitting constant and a slightly larger effect on the α-hydrogen splitting of the 1-alkyl group (Table III).

The most important conclusion to be derived from these results is that the 1-alkyl-4-carbomethoxypyridinyl radical is not very polar, since a much larger change in splitting constants or spectral width would have been expected for a radical in which charge separation was important.[26] The conclusion is in agreement with a previous opinion based on (a) solubility of the radicals in very nonpolar solvents, like hexane, and (b) kinetic results for atom-transfer reactions in solvents of different polarity.[6,7]

Dimerization (π-merization). Three properties reflect the changes due to dimerization of pyridinyl radicals (eq 7). These are (a) the loss of EPR signal strength, (b) the growth of a visible absorption band, and (c) loss of volatility.

$$\mathrm{Py}\cdot + \mathrm{Py}\cdot \rightleftharpoons \underset{\text{singlet}}{(\mathrm{Py}\cdot)_2} \rightleftharpoons \underset{\text{triplet}}{(\mathrm{Py}\cdot)_2} \qquad (7)$$

The methyl, ethyl, and isopropyl radicals all show very large losses in EPR signal strength on cooling to 77 K in MTHF. The changes parallel the appearance of a strong visible absorption close to the location of the weak visible absorption of the monoradical. The *tert*-butyl derivative also shows a decrease in EPR signal strength down to 195 K. Preponderant π-mer formation for 1-methyl-, 1-ethyl-, and 1-isopropyl-4-carbomethoxypyridinyls in MTHF at low temperature gives way to modest π-mer formation for the 1-*tert*-butyl radical.

The relative volatility observed for the radicals is suggestive of an order of association, combined with an effect of molecular weight: isopropyl > ethyl > *tert*-butyl $\simeq$ methyl.

The triplet dimer in equilibrium with the singlet dimer occurs for the 1-methyl, 1-ethyl, and 1-isopropyl radicals but apparently not for the 1-*tert*-butyl radical (eq. 7). Ikegami and co-workers have reported the production of isomeric triplet dimers on irradiation, and have proposed some difference in structure on the basis of zero-field splitting parameters.[19,27]

Stability. The survival of pyridinyl radicals is a practical fact of great utility in the study of the chemical and physical properties of pyridinyl radical and diradicals.[4] Our studies show that very high concentrations of free radical (2 M) favor decomposition. Dilute solutions in acetonitrile are very stable. At present, there is no evidence for dimerization to a compound with a localized covalent bond and no information on the products of decomposition of the free radicals in nonaqueous solvents.

Reactivity toward Halocarbons. There is essentially no effect of the 1-alkyl group on the rate of bromine atom transfer from bromochloromethane to pyridinyl radical. The products of the reaction with the 1-isopropylpyridinyl radical and bromochloromethane show that the sum of reactivities of the 2 and 6 positions are about equal to that of the 4 position, approximately what might have been expected on the basis of the spin densities estimated for these positions on the basis of EPR spectra.[4]

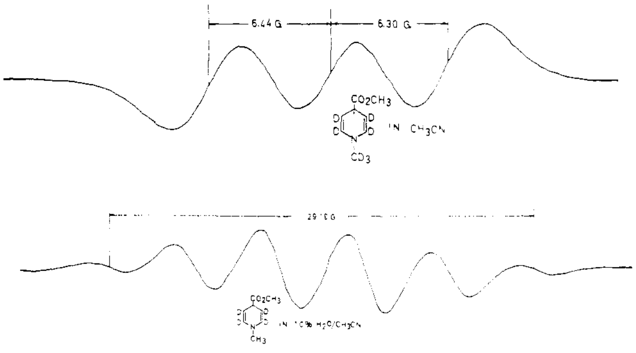

Figure 2. EPR spectra of (a) 1-trideuteriomethyl-4-carbomethoxypyridinyl-d_4 and (b) 1-methyl-4-carbomethoxypyridinyl-d_4 in 2-methyltetrahydrofuran. The splitting constant for the nitrogen is derived from the spectrum as shown in a.

Experimental Section

Solvents. Acetonitrile (spectroquality, Matheson, Coleman and Bell, E. Merck, Darmstadt) was degassed and stored over previously gassed (24 h, 1 × 10^5 Torr, 450 °C) molecular sieves (4A) (Linde Co.). Degassed solvent was distilled onto a mixture of magnesium turnings and 1,1′-trimethylenebis(4-carbomethoxypyridinium) diiodide (the magnesium complex of the bis(pyridinyl) diradical thus generated is highly reactive toward oxygen and possible other impurities[11]) before distillation into the desired apparatus or storage tube. This method gives routinely pure CH_3CN (no radical-reactive impurities). It has been used for small quantities of CD_3CN and appears to be the best purification method for CH_3CN for vacuum line use. 2-Methyltetrahydrofuran (MTHF) (Eastman Organic, Fluka) was refluxed over sodium for 10 days and then distilled. The material was degassed, distilled onto sodium and anthracene and, when needed, into a reaction apparatus.

Spectroscopic Measurements. UV–Vis. Cary Model 14 or 17 spectrophotometers were used.

Salts. 1-Methyl-4-carbomethoxypyridinium iodide, two crystallizations from methanol, mp 189–190 °C (dec) (in bath 184 °C), lit.[24] 190–191 °C (dec) (in bath 184 °C). 1-Ethyl-4-carbomethoxypyridinium iodide: mp 110–111 °C (lit.[24] 111–112 °C). 1-Isopropyl-4-carbomethoxypyridinium iodide. Isopropyl iodide (44 g, 0.26 mol) and methyl isonicotinate (4-carbomethoxypyridine) (30 g, 0.22 mol) were refluxed for 27 days in a mixture of acetone (25 cm^3)–ethyl ether (200 cm^3), yielding the yellow salt (1.7 g, 2.4% yield) in pure form, mp 134–136 °C. Anal. Calcd for $C_{10}H_{14}NO_2I$: C, 39,10; H, 4.60; N, 4.56; I, 41.32. Found: C, 39.40; H, 4.58; N, 4.43; I, 41.53. Less pure material, mp 129–134 °C, formed in 25% acetone–ether but could not be further purified. Pure reactants warmed to 35–40 °C gave salt, mp 130–132 °C.

1-*tert*-Butyl-4-carbomethoxypyridinium iodide-1-(2,4-dinitrophenyl)-4-carbomethoxypyridinium *p*-toluenesulfonate[14] (3.8 g, 8.0 mmol) in methanol (50 cm^3) was added dropwise to a solution of *tert*-butylamine (730 mg, 10.0 mmol) in methanol (10 cm^3). After addition, stirring 2 h, and removal of most of the solvent, the mixture was poured into ether (500 cm^3) and the precipitate was filtered off and dried. The 1-*tert*-butyl-4-carbomethoxypyridinium *p*-toluenesulfonate (1.6 g, 4.4 mmol) was dissolved in acetone (300 cm^3) and mixed with sodium iodide (0.75 g, 5.0 mmol) in acetone (100 cm^3). Sodium *p*-toluenesulfonate was filtered off, the solvent was removed, and the residue was crystallized from isopropyl alcohol–acetone to give yellow crystals of iodide salt: mp 175–180 °C, yellow–red, 185–190 °C (dec); equiv wt calcd 321; found 315.5. NMR (D_2O) δ 1.8 (s, 9 H) (*t*-Bu), 4.0 (s, 3 H) (ester CH_3), 8.72 (d, 2 H) (3,5-H on ring), 9.55 (d, 2 H) (2,6-H on ring). Charge-transfer bands: (CH_2Cl_2) concn λ_{max} (ϵ_{max}) 8×10^{-4}, 441.7 (980); 14×10^{-4}, 441.2 (1000); 23×10^{-4}, 440.0 (1070); 52×10^{-4}, 438.0 (1090) (*i*-PrOH) 15×10^{-4}, 382.0 (322). These charge-transfer bands occur at slightly lower energies than those for 1-ethyl-4-carbomethoxypyridinium iodide:[24] (CH_2Cl_2) 20×10^{-4}, 438.1 (1150); (*i*-PrOH) 26×10^{-4}, 374.7 (532).

Pyridinyl Radicals. Sodium amalgam reduction according to the procedure of Kosower and Waits[17] was suitable for the preparation of all four 1-alkyl-4-carbomethoxypyridinyl radicals. However, the reactivity of the methyl radical was such that the reduction had to be carried out between −30 and −40 °C. All of the radicals could be distilled as noted in the text. However, the *tert*-butyl radical was contaminated with a volatile substance with absorption at 260 nm, thought to be *tert*-butyl iodide (volatility, light absorption). The *tert*-butyl radical was therefore extracted from the reduction mixture (30 min, 0 °C) with benzene, the benzene was removed after filtration, the radical was extracted with isopentane, the solution was filtered, the isopentane was removed, and acetonitrile was introduced. No volatile impurity was seen in the extraction procedure. All operations were carried out in all-glass apparatuses with complete exclusion of oxygen. Final solutions were normally stored at −10 °C in a number of tubes carrying breakseals for further investigations.

Kinetics Studies. (a) Reaction with Bromochloromethane. Solutions containing approximately 5×10^{-3} M radical in acetonitrile were mixed with sufficient bromochloromethane to produce a ~1 M solution of halocarbon. The decrease in the visible absorption peak was followed at 25 °C. At the end of the kinetic run, the halocarbon concentration was determined by GLC. Data fitted first-order kinetics to more than 60% reaction. Results are recorded in Table II.

(b) Thermal Stability. Large amounts of radical were prepared and transferred in acetonitrile as solutions approximately 0.15 M in radical, since all of the radicals were moderately stable at this concentration. The solutions were concentrated to approximately 2 M and transferred to an apparatus carrying a specially made quartz cell with 0.005-cm path length and openings at both top and bottom. The course of decomposition was followed at the maximum in the visible. Deviations from Beer's law were readily noted, the absorption being about twice as great as expected at the high concentration at 25 °C. The change in optical densities did not fit either first- or second-order kinetics, but approximate times for the half-decomposition of each radical could be obtained as follows: 1-methyl-4-carbomethoxypyridinyl (~1 h), 1-ethyl radical (~13 h), 1-isopropyl radical (≫100 h), 1-*tert*-butyl radical (≫150 h). At 75 °C, the isopropyl radical increased in absoprtion at 630 nm ($t_{1/2}$ 5–6 h) and then decreased after 30 h. A new absorption band at 480 nm increased with a $t_{1/2}$ of about 20 h.

Product Studies. Reaction of 1-isopropyl-4-carbomethoxypyridinyl with bromochloromethane. An acetonitrile solution of isopropyl radical (100 cm^3, 0.0376 M) was mixed with bromochloromethane (15 cm^3) (Kodak, degassed on line). Color change showed that the reaction was complete within 4.5 h. The solvent was removed and the residue was extracted twice with cyclohexane (30 cm^3)–benzene (10 cm^3). A brown solid residue, mp 60–98 °C, was shown to be somewhat impure 1-isopropyl-4-carbomethoxypyridinium bromide (0.310 g, 34.9%); NMR (D_2O) δ 1.69 (6 H, d) ($(CH_3)_2CH$), 4.00 (3 H, s) (CH_3O), 5.20 (1 H, heptet) (CHN), 8.52 (2 H, d) (3,5-H), 9.15 (2 H, d) (2,6-H); UV λ_{max} 220, 274 nm; IR almost identical to that for iodide salt. Solvent of extract was removed and oxygen-free acetone-d_6 was used to dissolve the residue, ~0.35 g (81% yield for chloromethyldihydropyridine): NMR two almost equal sets of doublets, centered at λ 1.25 and 1.30, represented the isopropyl groups of two isomeric products (δ 3.70 and 3.80), the methyl groups of the CH_3OOC– groups of two isomeric products, and (δ 4.5 and 6.1) unresolved peaks expected for a mixture of two dihydropyridines. The NMR had to be taken soon after the separation procedure described above because of the thermal instability of the products; their reactivity toward oxygen also made the experiment troublesome to execute.

EPR Studies. Solutions of radicals in MTHF were adjusted to approximately 0.05 M using the visible absorption band. Concentrations are thus approximate due to (10–20%?) dimerization, with a consequent increase in visible absorption. These solutions were used for evaluation of triplet dimer content. There were no obvious differences in triplet dimer signal strength between rapidly cooled and annealed samples. Solutions of ca. 10^{-4} M were used for high-resolution EPR spectra. The *tert*-butyl radical exhibited the same EPR spectrum at 10^{-3} M and 8.4×10^{-5} M at 25 °C.

Hydrogen Abstraction. Attempts to demonstrate hydrogen abstraction by 1-isopropyl-4-carbomethoxypyridinyl radical (ca. 0.01 M) in acetonitrile were carried out for a number of good hydrogen donors. 9,10-Dihydroanthracene (0.125 M): 11.5% decrease in the visible absorption in 96 h at 25 °C; 5% decrease after 6 h at 60 °C. 1-Benzyl-3-carbamido-1,4-dihydropyridine (0.125 M): 13% decrease, 25 °C, 96 h; 6% decrease, 60 °C, 6 h. Cumene (0.125 M): 17 h, 25 °C, no change; 6% decrease, 5.5 h, 60 °C. 1-Dodecanethiol (0.1 M): slow reaction, 25 °C, approximate $k = 3.3 \times 10^{-6}\ s^{-1}$.

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Registry No.— **4,** 64714-75-6; **4a,** 64754-22-9; **4b,** 64754-23-0; **5,** 64714-76-7; 1-isopropyl-4-carbomethoxypyridinium iodide, 15012-99-4; isopropyl iodide, 75-30-9; methyl isonicotinate, 2459-09-8; 1-*tert*-butyl-4-carbomethoxyridinium iodide, 64714-71-2; 1-(2,4-dinitrophenyl)-4-carbomethoxypyridinium *p*-toluenesulfonate, 53365-04-1; *tert*-butylamine, 75-64-9; 1-*tert*-butyl-4-carbomethoxypyridinium *p*-toluenesulfonate, 64714-73-4; bromochloromethane, 74-9705; 1-isopropyl-4-carbomethoxypyridinium bromide, 64714-74-5.

References and Notes

(1) (a) Tel-Aviv University. (b) State University of New York, at Stony Brook.

(2) The conditions and time scale of the experiment define the experimenter's view of the stability of the radical. For a radical to be "stable" under a particular set of conditions means that the radical "persists" long enough to be manipulated and measured. We reserve the term "stable" for radicals which can be isolated in reasonably pure form. In the case of 1-alkyl-4-carbomethoxypyridinyls, stability can be considerable in the absence of oxygen, a finding confirmed for differently substituted pyridinyl radicals by M. Itoh and S. Nagakura, *Bull Chem. Soc. Jpn.*, **39,** 369 (1966), A. R. Katritsky and F. Soti, *J. Chem. Soc., Perkin Trans. 1,* 1427 (1974), and Y. Ikegami, personal communication.
For a different emphasis of meaning, the reader might consult D. Griller and K. U. Ingold, *Acc. Chem. Res.*, **9,** 13 (1976), but should he wish to make a choice between the two terms, he might do well to consider the first definition of the word persist (ref 3) "to be obstinately repetitious, insistent or tenacious in some activity".

(3) The American Heritage Dictionary of the English Language, W. Morris, Ed., American Heritage-Houghton Mifflin, Boston, 1969, p 978.

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