DERIVATIVES OF N-OXYL- AND N-OXOPIPERIDYLACETIC ACIDS

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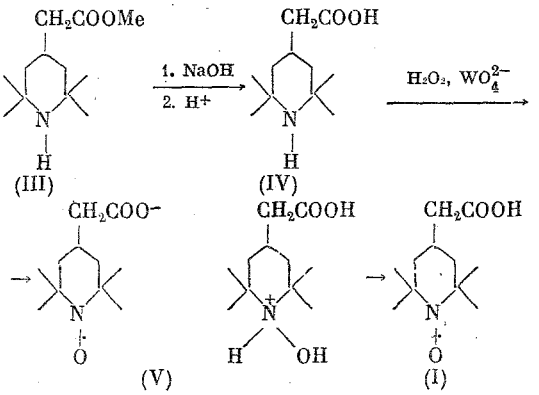
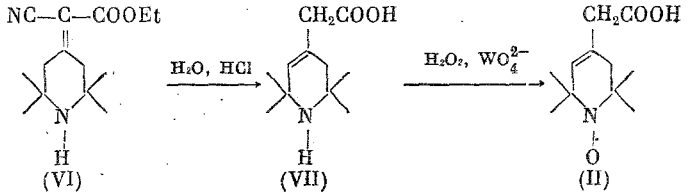
Carboxy derivatives of pyrroline- and pyrrolidine-1-oxyls are commonly used as acylating and carbamoylating spin labels [1-3]. The use of piperidine-oxyls is limited by their unavailability. However, six-membered ring spin labels have a number of advantages relative to their five-membered analogs. In the present communication, we give a synthesis for derivatives of N-oxylpiperidylacetic acids (I) and (II) and the result of the oxidation of (I) and (II) to the corresponding oxoammonium salts.

N-Oxylpiperidylacetic acid (I) was obtained by a reported method from methyl piperidylacetate (III) [4, 5]



The optimal conditions for the oxidation of acid (IV) [6] are: pH 11-11.5, $[H_2O_2] \approx 0.1$-0.2 mole/liter and $[WO_4^{2-}] \approx 0.01$ mole/liter. At about 20°C, the reaction is complete in about 36 h. The reaction rate drops sharply with a reduction in pH or H_2O_2 concentration while the rate of decomposition of H_2O_2 increases sharply with an increase in pH and the H_2O_2 concentration. The corresponding N-hydroxypiperidylacetic acid is an intermediate in the oxidation of (IV) and precipitates from the ethereal extract in the case of the incomplete oxidation of (IV) to (I) as pink salt (V). The structure of (V) was indicated by ESR analysis for $\rangle N^{\cdot}-O$ content, IR spectroscopy, and potentiometric titration. The latter gives a two-step curve with inflections at 4.7 and 7.2 which correspond to pK_a of the carboxyl and $\rangle \overset{+}{N}HOH$ groups. The IR spectrum has bands at 2100-2700 cm^{-1} (CO_2H and $\rangle \overset{+}{N}HOH$), 1707 cm^{-1} (C=O), and 1405 and 1610 cm^{-1} (CO_2^-). The formation of stable salt (V) indicates the greater acidity of the carboxylic acid group of radical (V) relative to the corresponding hydroxylamine. N-Oxyltetrahydropyridylacetic acid (II) was obtained from 4-carboethoxycyanomethylene-2,2,6,6-tetramethylpiperidine (VI) [4]:



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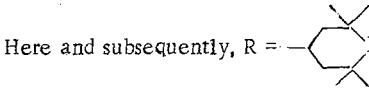
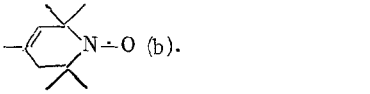
Tetrahydropyridylacetic acid (VII) formed upon the hydrolysis of (VI) is used for the subsequent steps without separation from the reaction side products. The oxidation of (VII) was carried out under the same conditions as (IV). Acid (II) crystallizes from H_2O and D_2O as a monohydrate (II•H_2O) and deuterohydrate of the deuteroacid (II-D•D_2O) which are stable in the air. Upon drying in vacuum, the hydrates are converted into anhydrous acids (II) and (II-D), respectively.

Acids (I) and (II) react with ethyl chloroformate or the bischloroformate of ethyleneglycol in the presence of triethylamine to give mixed anhydrides (VIII) and (IX)

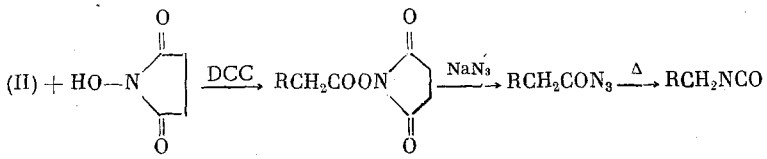
$RCH_2COOCOOEt$, (VIII a, b) $\quad RCH_2COOCO(CH_2)_2OOCOOCCH_2R$ (IX a, b)

Here and subsequently, R =  (a),  (b).

Anhydrides (VIII) and (IX) are viscous red oils which decompose upon distillation. They may be used as acylating reagents without separation from the reaction solution. Anhydrides (VIIIa) and (IXa) react with NaN_3 to yield azide (Xa) which upon heating is converted virtually quantitatively to isocyanate (XIa)

$$(IXa) \xrightarrow{NaN_3} \underset{(Xa)}{RCH_2CON_3} \xrightarrow[-N_2]{\Delta} \underset{(XIa)}{RCH_2NCO}$$

Isocyanate (XIb) could not be obtained by this scheme in satisfactory yield from anhydrides (VIIIb) and (IXb). Isocyanate (XIb) was obtained in good yield through activated ester (XIIb), as follows:



(XIIb) (Xb) (XIb)

Ester (XIIb), which is formed in quantitative yield in the reaction of acid (II) with N-hydroxysuccinimide in the presence of dicyclohexylcarbodiimide (DCC) is an efficient acylating reagent. It reacts readily with NaN_3 to give azide (Xb) which, upon heating, yields isocyanate (XIb). Isocyanates (XIa) and (XIb) are nonvolatile red liquids which may be distilled in vacuum and are stable upon heating at less than 150°C. These compounds react with aniline to give high-melting, highly crystalline ureas (XIIIa) and (XIIIb)

$$(XIa, b) + PhNH_2 \rightarrow \underset{(XIIIa, b)}{RCH_2NHCONHPh}$$

Solutions of (XIa) and (XIb) which are formed upon the decomposition of azides (Xa) and (Xb) may be used for carbamoylation without further purification.

The structure of all the radicals obtained was confirmed by elemental analysis and spectral methods. The characteristic IR bands are given in Table 1. The mass spectra of (I), (II), and their derivatives, with the exception of (IX), have M^+ molecular ion peaks as well as fragmentation ions which are characteristic for piperidine nitroxyls: $[M - Me]^+$, $[M - CH_2O]^+$, $[M - NO]^+$, $[M - NO - Alk]^+$, and $[M - NO - Me_2CCH_2]^+$. Molecular ions are not found in the mass spectra of mixed anhydrides (IXa) and (IXb). These compounds give strong peaks for $[M - C_4H_4O_5]^+$ ions which correspond to anhydrides of acids (I) and (II) and are formed by the loss of the $C_4H_4O_5$ groups from M^+ or upon the ionization of anhydrides obtained upon the pyrolysis of (IXa) and (IXb). The ESR spectra of dilute solutions of (I) and (II) and their monoradical derivatives consist of three lines, while the spectra of biradicals (IXa) and (IXb) consist of five lines. The hyperfine coupling constants a_N for (I) and its derivatives are approximately the same

TABLE 1. IR and UV Spectra of Piperidylacetic Acid Derivatives

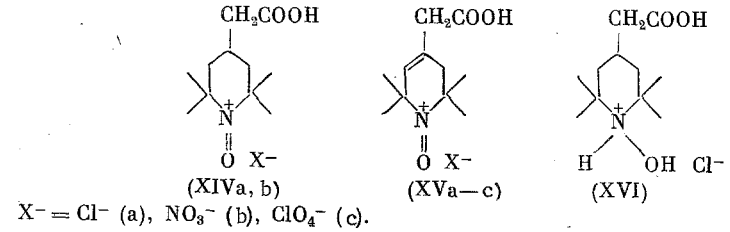
Compound	IR spectrum*		UV spectrum		
	ν, cm^{-1}	group	solvent	λ_{max}, nm	ε, liters/mole · cm
(I)	1708	C=O	Ehtanol	451	11
	2566, 2620, 2674, 2716 и 3035	COOH		243	3600
(II)	1726 and 1740	C=O	Ethanol	434	7,4
	2440, 2517, 2576, 2652, 2730 and 3076	COOH		231	2700
	1690	C=C			
(XIa)	2275	N=C=O	MeCN	463	10,5
				242	2900
(XIb)	2275	N=C=O	MeCN	446	7,6
	1667	C=C		234	3000
(XIIb)	1730, 1747	C=O (ester)	MeCN	445	7,4
	1779, 1809	C=O		221 sh	3000
(XIIIa)	1501, 1537, 1595	C=C(Ph)	Ethanol	449	10,4
	1695, 1749, 1874, 1947	Ph		284 sh	1800
	3031, 3042, 3074	C–H(Ph)		275 sh	2900
	1577, 3115, 3187, 3329	N–H		267 sh	3600
	1638	C=O		241	35000
(XIIIb)	1500, 1542, 1595	C=C(Ph)	Ethanol	432	7,9
	1702, 1749, 1873, 1948	Ph		284 sh	1500
	3026, 3044, 3074	C–H(Ph)		275 sh	2400
	1574, 3110, 3191, 3320	N–H		269 sh	2800
	1643	C=O		241	28000
(XIVa)	1203, 2479, 2515, 2566	COOH	H_2O	504 sh	15
	2594, 2652, 2720			477	21
	1702, 1712	C=O		464	21
	1613	$\overset{+}{N}$=O		230	1900
(XIVb)	1207, 2480, 2565, 2670, 2740	COOH	H_2O	503 sh	15
	1710, 1720	C=O		479	22,5
	1623	$\overset{+}{N}$=O		466	22
	721, 827, 1037, 1309, 1412	NO_3^-		244 sh	2050
(XVa)	1202, 2452, 2540, 2606		H_2O	472 sh	86
	2647, 2674, 2727	COOH		417	110
	1698	C=O			
	1674	C=C		237 sh	1800
	1611	$\overset{+}{N}$=O			
(XVb)	1190, 2337, 2495, 2578, 2702	COOH	H_2O	485 sh	77
	1720	C=O		395	130
	1627	$\overset{+}{N}$=O		247 sh	1700
	714, 827, 1039, 1310, 1414	NO_3^-			
(XVc)	1236, 2455, 2555, 2650, 2743	COOH	H_2O	470 sh	87
	1712	C=O		417	110
				237sh	2100
	1630	$\overset{+}{N}$=O	MeCN	471 sh	98
	623, 932, 1087	ClO_4^-		420	120
				227 sh	2100

*The spectra for the liquids are given for (XIa) and (XIb); the spectra of vaseline mulls are given for the other compounds.

and equal to 16.2 ± 0.2 Oe in ethanol and 15.5 ± 0.2 Oe in benzene; the values for a_N are less for unsaturated acid (II) and its derivatives and are equal to 15.7 ± 0.2 Oe in ethanol and 15.1 ± 0.2 Oe in benzene.

The bands at 430-450 and 230-240 nm correspond to the nitroxyl group in the UV spectra of the radicals (see Table 1). These bands are shifted toward shorter wavelengths for unsaturated acid (II) and its derivatives, while the intensity of the long-wavelength band is less by a factor of 1.4 than for (I). The UV spectra of ureas (XIIIa) and (XIIIb) show absorption for the $\rangle N\dot{-}O$ group and for the benzene chromophore (see Table 1).

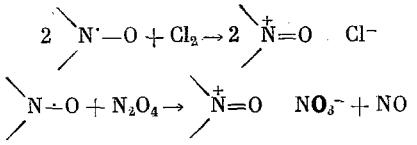
N-Oxylpiperidylacetic acids (I) and (II) are readily oxidized by the action of Cl_2 and N_2O_4 to the corresponding oxoammonium salts (XIV) and (XV)



(XIVa, b) (XVa—c) (XVI)

$X^- = Cl^-$ (a), NO_3^- (b), ClO_4^- (c).

In an inert atmosphere at −20°C, the stoichiometry of these reactions corresponds to the following equations



Oxoammonium salts (XIV) and (XV) are orange or red-brown crystalline compounds. Unsaturated salts (XV) have deeper color and lower decomposition temperature. The anion in salts (XIV) and (XV) may be replaced by exchange. Thus, insoluble perchlorate (XVc) crystallizes upon the addition of perchloric acid to an aqueous solution of (XVa). In aqueous solution, salts (XIV) and (XV) slowly decompose to give the starting radicals and a mixture of unidentified products. The rate of decomposition increases rapidly with an increase in pH. Alcohols rapidly and quantitatively reduce (XIV) and (XV) to the corresponding hydroxypiperidinium salts, such as (XVI).

The frequencies of the stretching vibrations of the $\rangle\overset{+}{N}{=}O$ group in the IR spectra of oxoammonium salts (XIVa) and (XVa) are about 15 cm^{-1} less than in the case of the corresponding nitrates and perchlorates due to a strong interaction between the cations and the chloride anion. The UV spectra of aqueous solutions of salts (XIVa) and (XIVb) have two bands due to the oxopiperidinium cation (see Table 1). The long-wavelength band has indistinct vibrational structure. The short-wavelength band of the cation is the spectrum of nitrate (XIVb) is partially superimposed by the absorption of the nitrate anion and is seen as a shoulder. The long-wavelength band of the cation in the spectra of unsaturated salts (XVa-c) is strongly shifted toward shorter wavelengths and its intensity is about five times greater than in the case of (XIV). Such a change in the spectrum indicates a strong interaction of the formally unconjugated $\rangle\overset{+}{N}{=}O$ and C=C groups. This interaction is characteristic for β,γ-unsaturated ketones with favorable steric conditions for overlap of the π- and n-orbitals of the carbonyl group with the π-orbitals of the C=C bond [7].

EXPERIMENTAL

The IR spectra were taken on a Specord 75-IR spectrometer. The UV spectra were taken on a Specord UV-VIS spectrometer and the ESR spectra were taken on an EPA-2M radiospectrometer. The mass spectra were taken on an LKB-9000 spectrometer at 70 eV ionizing electron energy and 250-270°C ionization chamber temperature. The melting points were determined on a PNMK heating block manufactured in East Germany.

4-Carboxymethyl-2,2,6,6-tetramethylpiperidine-1-oxyl (I). A solution of 59.6 g methyl 2,2,6,6-tetramethylpiperidyl-4-acetate (III) and 12 g NaOH in 200 ml 50% ethanol was heated at reflux for about 1 h until the completion of hydrolysis. The reaction was monitored by potentiometric titration. The excess alkali was neutralized with 2 N HCl to pH 11-11.5 and 0.6 g $Na_2WO_4 \cdot 2H_2O$ and 0.1 g Trilon B were added to the solution. Then, 60 ml 30% H_2O_2 was added at about 20°C with stirring in 5-ml portions over gradually increasing time intervals from 1 h initially to 3 h at the end of the reaction. The extent of amino oxidation was monitored relative to the accumulation of $\rangle N\dot{-}O$ groups by ESR spectroscopy and by potentiometric titration to determine consumption of the substrate and the intermediate $\rangle$NOH group [6]. After completion of the reaction in about 36 h, the reaction solution was washed with

three 50-ml portions of ether and acidified with ice cooling and rapid stirring using 2 N HCl to pH 3. The red oil formed was extracted with four 50-ml portions of ether and the extract was dried over Na_2SO_4 and evaporated in vacuum to yield 49.9 g (84%) (I) as red prisms with mp 98-99°C (from 4:1 hexane–chloroform).

4-Carboxymethyl-2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridine-1-oxyl (II). A sample of 50 g 4-carboethoxycyanomethylene-2,2,6,6-tetramethylpiperidine (VI) was heated at reflux for 15 h with 375 ml conc. HCl. Removal of the HCl in vacuum left a mixture of the hydrochloride salt of 2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridyl-4-acetic acid (VII) and NH_4Cl which was dissolved in 150 ml water and made basic with 30% NaOH to pH 11. Then, 0.74 g $Na_2WO_4 \cdot 2H_2O$ and 0.1 g Trilon B were added to this solution, followed by 42.5 ml 30% H_2O_2 by the above procedure. After completion of the reaction, the solution was acidified with 2 N HCl to pH 3 and ice cooling to yield 24.2 g (53%) acid (II) monohydrate as orange platelets with mp 59-65°C. Found: H_2O, 7.9 ± 0.2%. $C_{11}H_{18}NO_3 \cdot H_2O$. Calculated: H_2O, 7.82%. IR spectrum (vaseline oil, ν, cm^{-1}): 1640, 1910, 2180, 3260, 3360, and 3455 (H_2O), 1710 (C=O), 1688 (C=C), 1237, 2540, 2602, and 2715 (CO_2H). Upon drying at 1 Pa for about 30 min at 56°C, the hydrate is converted into anhydrous acid (II) which crystallizes from ether as orange prisms with mp 72-73°C. Found: C, 63.0 ± 0.007; H, 8.64 ± 0.07; N, 6.9 ± 0.1%, m/z 212 (M^+). $C_{11}H_{18}NO_3$. Calculated: C, 62.24; H, 8.55; N, 6.60% molecular weight 212.27. The monodeuterohydrate (II-D•D_2O) is formed with mp 60-65°C upon the recrystallization of (II) from D_2O. IR spectrum (vaseline oil, ν, cm^{-1}): 2403, 2480, 2565 (D_2O), 1714 (C=O), 1688 (C=C), 1078, 1905, 1956, 2055, and 2195 (CO_2D).

2,2,6,6-Tetramethyl-4-(succinimidooxycarbonylmethyl)-1,2,5,6-tetrahydropyridine-1-oxyl (XIIb). A solution of 1.03 g of dicyclohexylcarbodiimide in 15 ml ethyl acetate was added to a solution of 1.06 g (II) and 0.58 g N-hydroxysuccinimide in 10 ml dry ethyl acetate and stirred for 2 h without cooling. The dicyclohexylurea precipitate was filtered off and the filtrate was evaporated in vacuum to yield 1.45 g (94%) (XIIb) as yellow needles with mp 129-131°C (from 50% ethanol). Found: C, 58.7 ± 0.3; H, 7.0 ± 0.1; N, 9.4 ± 0.1%; m/z 309 (M^+). $C_{15}H_{21}N_2O_5$. Calculated: C, 58.24; H, 6.84; N, 9.06%; molecular weight, 309.34.

4-Isocyanatomethyl-2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridine-1-oxyl (XIb). A solution of 0.65 g NaN_3 in 4 ml H_2O was added dropwise to a solution of 1.55 g (XIIb) in 20 ml acetone at 0°C with stirring. The reaction mixture was stirred for 2 h at 0°C and poured onto 50 g crushed ice and azide (Xb) was extracted with three 10-ml portions of cyclohexane. The extract was washed with ice water, dried over Na_2SO_4, heated at reflux for 30 min, and the solvent was removed in vacuum to yield 0.76 g (73%) (XIb) as a red-orange oil which distills at 85-90°C bath temperature at 2-Pa pressure.

Mixed Anhydrides (VIII) and (IX). A solution of 2.5 mmoles ethyleneglycol bischloroformate or 5 mmoles ethyl chloroformate in 5 ml of the corresponding solvent was added dropwise to a solution of 5 mmoles (I) or (II) in 15 ml dry ether or acetone with cooling to from −5° to 0°C and stirring. The reaction mixture was then stirred for 1 h without cooling and the $Et_3N \cdot HCl$ precipitate was filtered. The filtrate was evaporated in vacuum to give 90-95% yields of anhydrides (VIII) and (IX) as red oils. At $\geqslant$150°C, these compounds decompose rapidly and they cannot be purified by distillation in a vacuum $\geqslant$0.1 Pa.

4-Isocyanatomethyl-2,2,6,6-tetramethylpiperidine-1-oxyl (XIa). A solution of 0.49 g NaN_3 in 3 ml water was added dropwise to a solution of anhydride (IXa) in 15 ml obtained by the above procedure from 1.07 g (I) at 0°C. The reaction mixture was stirred for an additional 1 h at 0°C and then poured onto 30 g crushed ice and azide (Xa) was extracted with three 10-ml portions of cyclohexane. The extract was washed with two 10-ml portions of ice water, dried over Na_2SO_4, heated at reflux for 30 min, and evaporated in vacuum to yield 0.99 g (93%) (XIa) as a red oil with a characteristic odor which solidifies at $\leqslant$20°C, bp 130-135°C (4 Pa). Found: C, 62.5 ± 0.5; H, 8.8 ± 0.2; N, 13.4 ± 0.1%; m/z 211 (M^+). $C_{11}H_{19}N_2O_2$. Calculated: C, 62.53; H, 9.06; N, 13.26%; molecular weight 211.28.

Ureas (XIIIa) and (XIIIb). A solution of 2 mmoles aniline in 5 ml ether was added to a solution of 2 mmoles isocyanate (XIa) or (XIb) in 5 ml ether at about 20°C and stirred for 1 h. Then the solvent was removed in vacuum and the crystalline residue was washed with cyclohexane to give 96% (XIIIa) and 74% (XIIIb). Product (XIIIa) was obtained as pale pink platelets with mp 217-219°C (from dimethoxyethane). Found: C, 67.2 ± 0.3; H, 8.7 ± 0.1; N, 14.0 ± 0.2%; m/z 30 (M^+). $C_{17}H_{26}N_3O_2$. Calculated: C 67.08; H 8.61; N 13.80%; molecular weight 304.41. Product (XIIIb) was obtained as orange prisms with mp 186-188°C (from aceto-

nitrile). Found: C, 67.4 ± 0.3; H, 7.9 ± 0.1; N, 14.2 ± 0.2%; m/z 302 (M^+). $C_{17}H_{24}N_3O_2$. Calculated: C, 67.52; H, 8.00; N, 13.90%; molecular weight 302.395.

Oxopiperidinium Nitrates (XIVa) and (XVb). A solution of 2 mmoles (I) or (II) in 2 ml $CHCl_3$ was placed in a reactor with a porous bottom, argon was bubbled through the bottom, and 2 ml of a 1.15 M solution of N_2O_4 in chloroform was added at −20°C. The mixture was warmed to about 20°C. The crystalline salt precipitate was filtered off, washed with chloroform, and dried in vacuum. The yield of the salts was quantitative. Product (XIVb) was obtained as yellow prisms with decomposition temperature 127-129°C (from acetonitrile–ether). Found: N, 10.2 ± 0.1%. $C_{11}H_{20}N_2O_6$. Calculated: N, 10.14%. Product (XVb) was obtained as brick red platelets with a gold shine, decomposition temperature 88-90°C (from acetonitrile–ether). Found: C 48.2 ± 0.3; H, 6.6 ± 0.1; N, 10.1 ± 0.1%. $C_{11}H_{18}N_2O_6$. Calculated: C, 48.17; H 6.62; N 10.21%.

Oxopiperidinium Chlorides (XIVa) and (XVa) crystallize in quantitative yield upon the reaction of acids (I) and (II) with an equivalent amount of Cl_2 in CCl_4 at −20°C. Product (XIVa) was obtained as yellow prisms with decomposition temperature greater than 110°C (from acetic acid–ether). Found: N, 5.69%. $C_{11}H_{20}ClNO_3$. Calculated: N, 5.61%. Product (XVa) was obtained as brick red prisms with decomposition temperature 80-85°C (from acetonitrile–ether). Found: N, 5.72%. $C_{11}H_{18}ClNO_3$. Calculated: N, 5.65%.

4-Carboxymethyl-2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridinium Perchlorate (XVc). A sample of 1.5 ml 57% $HClO_4$ was added at 0°C with stirring to a solution of 0.31 g (XVa) in 3 ml water. The crystalline precipitate was washed with 0.5 ml ice water and five 3-ml portions of ether. Drying in vacuum gave 0.31 g (79%) (XVc) as orange prisms with decomposition temperature 159-162°C (from acetonitrile–dichloroethane). Found: N, 4.60%. $C_{11}H_{18}ClNO_7$. Calculated: N, 4.49%.

4-Carboxymethyl-2,2,6,6-tetramethyl-1-hydroxypiperidinium Chloride (XVI). Heating and rapid decoloration occur upon the addition of 0.25 g (XIVa) to 2.5 ml ethanol. Excess dry ether was added to the solution and the mixture was cooled to 0°C. The crystalline precipitate was filtered off, washed with dry ether, and dried in vacuum to yield 0.15 g (60%) (XVI) as colorless prisms with decomposition temperature 279-286°C (in a sealed capillary). Found: N, 5.43%. $C_{11}H_{22}ClNO_3$. Calculated: N, 5.56%. IR spectrum (Vaseline oil, ν, cm^{-1}): 1206 (CO_2H), 2473, 2512, 2564, 2620, 2656, 2700, and 2760 ($\overset{+}{N}HOH$ and CO_2H), 1725 (C=O). The multiple dissolution of (XVI) in D_2O and evaporation of the solution gives exchange of the H atoms by D atoms in the $\overset{+}{N}HOH$ and CO_2H groups and the formation of salt (SVI-D_3). IR spectrum (Vaseline oil, ν, cm^{-1}): 1035 (CO_2D), 1960, 2005, 2050, 2083, 2127, 2171, and 2235 ($\overset{+}{N}DOD$, CO_2D), 1720 (C=O).

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CONCLUSIONS

1. N-Oxylpiperidyl-4-acetic acids (I) and (II) yielded mixed anhydrides, hydroxysuccinimide esters, and isocyanates which may be used as acylating or carbamoylating spin labels.

2. The oxidation of N-oxylpiperidylacetic acids (I) and (II) by chlorine and N_2O_4 yields stable N-oxopiperidylacetic acid salts.

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