Preparation and Properties of Some Hydroxy Oximes and Their Precursors

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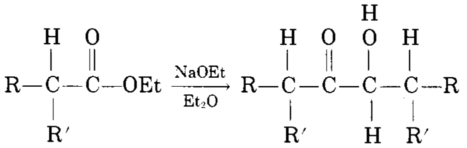
Three α-hydroxy oximes and a β-hydroxy oxime, as well as their respective hydroxy ketone precursors, were prepared and characterized by ir, nmr, and mass spectroscopy.

A few aliphatic α-hydroxy oximes have been cited in a recent patent (*6*), but no spectral data were provided. In this study, three α-hydroxy oximes and a β-hydroxy oxime—as well as their respective hydroxy ketone precursors—were prepared and characterized by ir, nmr, and mass spectroscopy. The β-hydroxy ketone described herein was previously reported by Cologne (*2*), but the corresponding oxime was not prepared. The literature appears to be devoid of spectral data on these classes of compounds.

EXPERIMENTAL

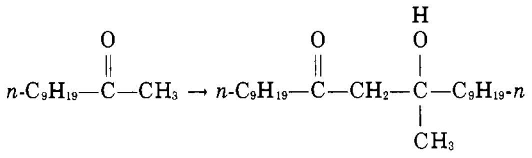
Hydroxy Ketones. The α-hydroxy ketones (compounds 1–3) were prepared by the acyloin condensation of the ethyl esters of the appropriate acids (*5*).



$$\mathrm{R{-}\overset{H}{\underset{R'}{C}}{-}\overset{O}{\overset{\|}{C}}{-}OEt \xrightarrow[Et_2O]{NaOEt} R{-}\overset{H}{\underset{R'}{C}}{-}\overset{O}{\overset{\|}{C}}{-}\overset{OH}{\underset{H}{C}}{-}\overset{H}{\underset{R'}{C}}{-}R}$$

Compound 1: R = n-C_4H_9, and R′ = C_2H_5
Compound 2: R = n-$C_4H_9CH(C_2H_5)$, and R′ = H
Compound 3: R = n-C_6H_{13}, and R′ = CH_3

The β-hydroxy ketone (compound 4) was synthesized via the aldol condensation of methyl n-nonyl ketone in the presence of N-methylanilinomagnesium bromide (*2*).



$$n\text{-}\mathrm{C_9H_{19}{-}\overset{O}{\overset{\|}{C}}{-}CH_3} \rightarrow n\text{-}\mathrm{C_9H_{19}{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}\overset{OH}{\underset{CH_3}{C}}{-}C_9H_{19}}\text{-}n$$

The preparation and properties of the hydroxy ketones are summarized in Table I.

Hydroxy Oximes. The hydroxy oximes (compounds 5–8) were prepared via oximation of the hydroxy ketones. In a typical reaction, the hydroxy ketone (0.1 mole) was mixed and hydroxylamine hydrochloride (0.2 mole) in ethanol (75 ml) with pyridine (75 ml) as the acid acceptor. The mixture was refluxed for 3 hr. The reaction mixture was cooled to room temperature, poured into 250 ml of water, and was extracted with ether. The ether layer was washed twice with dilute HCl, then neutralized with water. The ether solution was dried over anhydrous Na_2SO_4 and was evaporated in vacuo to afford the crude oxime. The α-hydroxy oximes were distilled, but the β-hydroxy oxime was thermally unstable, so it was chromatographed on silica gel using benzene–petroleum ether (1:1) as eluent.

The properties of the hydroxy oximes are summarized in Table I.

Spectral Data. Infrared spectra were obtained as liquid films with a Perkin-Elmer Model 137 spectrophotometer.

Table I. Hydroxy Ketones and Oximes[a]

Compd no.	Name	Starting material	Yield, %	Bp, °C (mm Hg)
1	5,8-Diethyl-7-hydroxydodecan-6-one	Ethyl 2-ethylhexanoate[b]	50	97–98 (0.1)
2	5,10-Diethyl-8-hydroxytetradecan-7-one	Ethyl 3-ethylheptanoate[c]	67	118–119 (0.07)
3	7,10-Dimethyl-9-hydroxyhexadecan-8-one	Ethyl 2-methyloctanoate[d]	61	123–125 (0.14)
4	12-Hydroxy-12-methylheneicosan-10-one[e]	Methyl n-nonyl ketone	65	. . .[f]
5	5,8-Diethyl-7-hydroxy-6-dodecanone oxime	Compound 1	35	133–134 (0.04)
6	5,10-Diethyl-8-hydroxy-7-tetradecanone oxime	Compound 2	70	158–159 (0.02)
7	7,10-Dimethyl-9-hydroxy-8-hexadecanone oxime	Compound 3	61	161–163 (0.06)
8	12-Hydroxy-12-methyl-10-heneicosanone oxime	Compound 4	20	. . .[g]

[a] Elemental analyses (C, H, N) in agreement with theoretical values were obtained and submitted for review. [b] Ref. *3*. [c] From 2-ethylhexanol, Ref. *4*. [d] From 2-bromooctane, Ref. *1*. [e] Ref. *2*, mp 23° C. [f] Dehydrated on attempted distillation; recrystallized from petroleum ether, mp 24° C. [g] Compound was thermally unstable during attempted distillation; purification was effected by chromatography on silica gel using benzene–petroleum ether (1:1) as eluent.

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Table II. Spectral Data

Compd no.	Infrared absorption, cm^{-1}/ (liquid films)			Nuclear magnetic resonance (chemical shift from TMS, ppm)			Mass spectra abundant fragments $(m/e)^a$
				Hydroxyl-H			
	(O—H)	(C=O)	(C=N)	in DMSO-d_6	in CCl_4	Oxime-H in DMSO-d_6	
1	3450	1580		3.8	3.4		$\underline{129}^b$ [$C_4H_9CH(C_2H_5)CHOH\oplus$], $\underline{127}$ [$C_4H_9CH(C_2H_5)CO\oplus$], $\underline{99}$ [$C_4H_9CH(C_2H_5)\oplus$]
2	3500	1600		4.7	4.7		172 [$C_4H_9CH(C_2H_5)CH_2CHOHCOH\oplus\cdot$], $\underline{143}$ [$C_4H_9CH(C_2H_5)CH_2CHOH\oplus$], $\underline{141}$ [$C_4H_9CH(C_2H_5)CH_2CO\oplus$], 99 [$C_4H_9CH(C_2H_5)\oplus$]
3	3475	1590		3.8	3.3		213 [$C_6H_{13}CH(CH_3)COCHOHCH(CH_3)CH_2\oplus$] 172 [$C_6H_{13}CH(CH_3)CHOHCOH\oplus\cdot$], $\underline{143}$ [$C_6H_{13}CH(CH_3)CHOH\oplus$], 97 [$C_7H_{13}\oplus$]
4	3500	1600		3.9	3.4		$\underline{213}$ [$C_9H_{19}COCH_2C(CH_3)OH\oplus$], 195 [$C_9H_{19}COCHC(CH_3)\oplus$], $\underline{171}$ [$C_9H_{19}C(CH_3)OH\oplus$], $\underline{155}$ [$C_9H_{19}CO\oplus$], 112 [$C_8H_{16}\oplus\cdot$]
5	3300		1650	^{c}		10.1	173 [$C_4H_9CH(C_2H_5)CHOHCNHOH\oplus\cdot$], 143 [$C_4H_9CH(C_2H_5)CNHOH\oplus\cdot$], 126 [$C_4H_9CH(C_2H_5)CN\oplus\cdot$], 111 [$C_4H_9C(C_2H_5)CH\oplus$], $\underline{99}$ [$C_4H_9CH(C_2H_5)\oplus$]
6	3300		1650	^{c}		10.1	187 [$C_4H_9CH(C_2H_5)CH_2CHOHCNHOH\oplus\cdot$], $\underline{156}$ [$C_4H_9CH(C_2H_5)CH_2CNOH\oplus$], 140 [$C_4H_9CH(C_2H_5)CH_2CHNH\oplus\cdot$], 110 [$C_8H_{14}\oplus\cdot$], 99 [$C_4H_9CH(C_2H_5)\oplus$]
7	3300		1650	^{c}		10.1	187 [$C_6H_{13}CH(CH_3)CHOHCNHOH\oplus\cdot$], 157 [$C_6H_{13}CH(CH_3)CNHOH\oplus\cdot$], 140 [$C_6H_{13}CH(CH_3)CHNH\oplus\cdot$], 110 [$C_8H_{14}\oplus\cdot$], 97 [$C_7H_{13}\oplus$]
8	3300		1650	^{c}		10.1	$\underline{228}$ [$C_9H_{19}C(CH_3)OHCH_2CNOH\oplus$], 185 [$C_9H_{19}C(CH_3)OHCH_2\oplus$], $\underline{170}$ [$C_9H_{19}CNOH\oplus$], 110 [$C_8H_{14}\oplus\cdot$]

[a] Low-intensity molecular ions as well as common low-mass hydrocarbon fragments were observed for all compounds. [b] Underlined mass ions indicate α-cleavage. Nonunderlined mass ions indicate β- or γ-cleavage, dehydration, hydrogen rearrangements, etc. [c] The hydroxyl protons were not well-defined in the oximes, primarily because of very low solubility of the oximes.

Nuclear magnetic resonance spectra were obtained using a Varian A-60 spectrometer. Mass spectra (70 eV) were obtained by direct sample inlet at 35° C into a Varian-MAT CH-4B mass spectrometer with ion source temperature at 250° C. Data are summarized in Table II.

LITERATURE CITED

(1) Cason, J., Rinehart, K. L., Thornton, S. D., *J. Org. Chem.*, **18**, 1594 (1953).

(2) Cologne, J., *Bull. Soc. Chim. Fr.* (5), **1**, 1101 (1934).

(3) Haüsermann, M., *Helv. Chim. Acta*, **34**, 2172 (1951).

(4) Levene, P. A., Rothen, A., Meyer, G. M., *J. Biol. Chem.*, **115**, 401 (1936).

(5) Snell, J. M., McElvain, S. M., *Organic Synthesis*, Coll. Vol. II, p 114 (1943).

(6) Swanson, R. R., U. S. Patent No. 3,224,873 (December 21, 1965).

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CORRECTION

The equation for density (Equation 9) reported in the article, "Electrical Conductance of the System LiCl-KCl-$CaCrO_4$," by R. P. Clark et al., [*J. Chem. Eng. Data*, **15**, 277 (1970)] should have read

$$\rho = -5.64 \times 10^{-4} t + 2.031 \tag{9}$$

As a result of this correction, Equation 11 was redetermined and now is

$$\log_{10} \Lambda = 4.53011 - 2.79403\,(10^3/T) + 5.38439 \log_{10} (10^3/T) \tag{11}$$

These changes cause small displacements of the curves in Figures 2 and 3. In addition, the value reported in Table II for Λ at 1.1 T_{fus} for the LiCl-KCl-$CaCrO_4$ eutectic should be 21.0 rather than 22.0.