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The 1-Hetera-3-cyclohexanone System. Carbon-13 Magnetic Resonance, Transannular Effects, and Conformational Analysis[1a]

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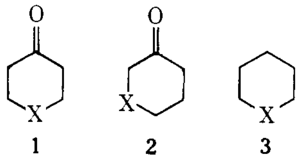
Carbon-13 (^{13}C NMR) magnetic resonance has been applied to the title compounds. Earlier suggestions[2,3] that the effects α to the heteroatom group reflect electrostatic effects and that the effects at a methylene carbon β to the heteroatom group indicate similar (chair) conformations are reinforced. The title compounds are therefore indicated to have chair conformations. Unusual heteroatom effects at the γ carbon are encountered. The groups appended to the heteroatoms are shown to have similar conformations in **1**, **2**, and **3** (under conditions of fast amide rotation). Transannular electron transfer is detected in the carbonyl chemical shifts of the thia analogue here and, to a lesser extent, in the 1-thia-4-cyclohexanone, modifying our earlier interpretation.[3] Other evidence for this transannular component is presented along with possible interpretations.

The use of carbon-13 nuclear magnetic resonance spectroscopy[2] (^{13}C NMR) as a probe[3] for conformational analysis[2–5] and transannular interactions[3] in six-membered heterocycles was evaluated in the 1-hetera-4-cyclohexanone system (**1**) in prior work. We wish herein to report an extension of this approach to the 1-hetera-3-cyclohexanone system (**2**), producing conclusions which reinforce earlier suggestions but which also require slight modification of our analysis of transannular interactions.

It has become fairly well-documented[2–6] that the effects of heteroatom groups on the α carbon reflect the heteroatom group electrostatic effects, and the 1-hetera-3-cyclohexanones (**2**) are no exception at either C-2 or C-6 (Figure 1). Plots of the chemical shifts (Table I) of the carbon resonances at C-2 and C-6 in **2** relative to the chemical shifts of the corresponding positions (α or γ to the carbonyl, respectively) in cyclohexanone ($\delta^{\alpha}_{C_5H_8XO} - \delta_{C_6H_{10}O}$) against the chemical shifts of the α carbons in the pentamethylene heterocycles[3] **3** relative



1 **2** **3**

a, X = S
b, X = N–CO–CH$_3$
c, X = N–CO–OR'
d, X = SO$_2$
e, X = N–CH$_2$Ph
f, X = N–CH$_3$
g, X = O
h, X = N–CO–C$_6$H$_5$

Table I. ^{13}C NMR Data[a] for 1-Hetera-3-cyclohexanones

compd	X	registry no.	solvent	C-2	C=O	C-4	C-5	C-6	other
2a	S	19090-03-0	$CDCl_3$	41.8	203.6	38.5	28.5	33.6	
2b	$NC(=O)CH_3$	34456-78-5	$CDCl_3$	*b*	205.0	38.2	*b*	*b*	*c*
2c	$NC(=O)OCH_3$	61995-18-4	$CDCl_3$	54.0	205.1	38.4	22.5	42.4	*d*
2c	$NC(=O)OCH_2CH_3$	61995-19-5	$CDCl_3$	54.0	204.9	38.4	22.6	42.4	*e*
2c	$NC(=O)OCH_2C_6H_5$	61995-20-8	$CDCl_3$	53.8	204.9	38.2	22.2	42.2	*f*
2d	SO_2	29431-37-6	$(CD_3)_2SO$	65.8	197.6	39.3	18.1	49.7	
2e	$NCH_2C_6H_5$	40114-49-6	$CDCl_3$	64.3	205.8	38.5	23.9	51.4	*g*
2f	NCH_3	5519-50-6	$CDCl_3$	66.4	205.9	38.0	24.1	53.9	*h*
2g	O	23462-75-1	$CDCl_3$	74.9	207.1	37.5	25.2	65.9	
2h	$NCOC_6H_5$	67452-85-1	$CDCl_3$	53.6	204.1	38.2	22.8	43.7	*i*

[a] Chemical shifts are in parts per million relative to internal Me_4Si. [b] Not available above coalescence temperature. [c] CH_3 not available above T_c; amide C=O, 169.4 ppm. [d] OCH_3, 52.8 ppm; amide C=O, 155.7 ppm. [e] OCH_2, 61.5 ppm; CH_3, 14.7 ppm; amide C=O, 155.2 ppm. [f] OCH_2, 67.2 ppm; amide C=O, 154.9; Ar, 136.4, 128.4, 128.0, and 127.8 ppm. [g] NCH_2, 62.3 ppm; Ar, 137.3, 128.7, 128.1, and 127.1 ppm. [h] NCH_3, 40.4 ppm. [i] Amide C=O, 170.0 ppm; Ar, 135.2, 129.7, 128.3, and 126.7 ppm.

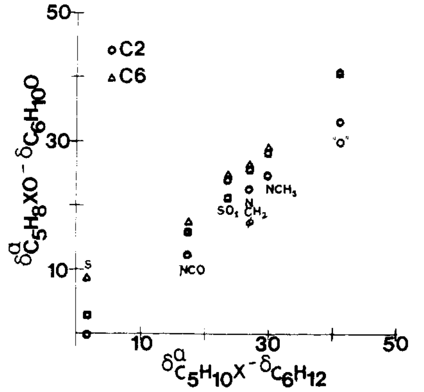


Figure 1. Comparison of the chemical shifts of the carbons α to the heteroatom in **3** (relative to cyclohexane) with the chemical shifts α to the heteroatom (relative to the appropriate position in cyclohexanone) (a) at C-2 in **2** (○), (b) at C-6 in **2** (△), and (c) in **1** (□).

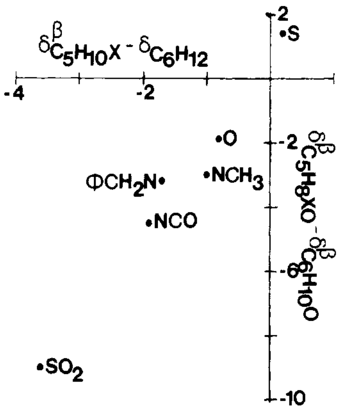


Figure 2. Comparison of the chemical shifts of the carbons β to the heteroatom in **3** (relative to cyclohexane) with the chemical shifts of the methylene carbons β to the heteroatom in **2** (relative to the position β to the carbonyl in cyclohexanone).

to cyclohexane ($\delta^{\alpha}{}_{C_5H_{10}X} - \delta_{C_6H_{12}}$) give good linear relationships for each carbon set: C-2, $Y = 0.855X - 0.604$ ($r = 0.985$); C-6, $Y = 0.810X + 5.525$ ($r = 0.989$). The correlations for C-2, for C-6, and for the α carbon in the 1-hetera-4-cyclohexanones[3] (**1**) ($Y = 0.980X - 0.916$ ($r = 0.988$)) are all roughly parallel, supporting the idea of a common origin for the α effect in heterogroup electronegativities. As before,[3,5] the α-substituent effects are in the order O ≫ NCH_3 > $NCH_2C_6H_5$ > SO_2 > NCO ≫ S, consistent with the relative electron-withdrawing abilities O > N > S. As may be noted in Table I, all of the amides and urethanes (**2b, 2c**, and **2h**) exhibit similar chemical shifts at all ring methylene carbons under conditions of rapid amide rotation.

When the chemical shifts of the carbons at C-5 in **2**, which are β to the heteroatom, relative to the corresponding position β to the carbonyl in cyclohexanone ($\delta^{\beta}{}_{C_5H_8XO} - \delta^{\beta}{}_{C_6H_{10}O}$), are plotted against the chemical shifts of the β carbons in the pentamethylene heterocycles[3] relative to cyclohexane ($\delta^{\beta}{}_{C_5H_{10}X} - \delta_{C_5H_{10}}$), another linear relationship is apparent (Figure 2): $Y = 2.619X + 0.475$ ($r = 0.986$). Following our earlier[3] suggestion that these β shifts may be the most useful quick probe of ring conformational preference, this linear relationship suggests that all of the 1-hetera-3-cyclohexanones (**2**) studied herein have similar (and presumably chair) ring conformations. The advantage of our "double difference" plot is again apparent. The linear relationships here and in Figure 1 indicate similar conformations of the mobile heteroatom appendages in **1, 2**, and **3**.

The situation at carbon 4, the carbon γ to the heteroatom group in **2**, is less clear. Comparison of these chemical shifts relative to the carbon α to the carbonyl in cyclohexanone ($\delta^{\gamma}{}_{C_5H_8XO} - \delta^{\alpha}{}_{C_6H_{10}O}$) with the chemical shifts γ to the heteroatom group in the pentamethylene heterocycles (**3**) relative to cyclohexane ($\delta^{\gamma}{}_{C_5H_{10}X} - \delta_{C_6H_{12}}$) produces a roughly horizontal correlation with high scatter. Such a line of roughly 0 slope would suggest that the heteroatom group has a constant influence at C-4 in **2** which is independent of the nature of the heteroatom group. This result would be unprecedented.[3,5-9] The high degree of scatter suggests the operation of several opposing factors, but the nature of the factors here (other than the traditional steric and electrostatic ones, which should not have resulted in high scatter) is unclear.

The remaining carbon to consider in **2** is the carbonyl carbon, which is β to the heteroatom group. When the chemical shift of the carbonyl carbons in **2** relative to the cyclohexanone carbonyl ($\delta^{C=O}{}_{C_5H_8XO} - \delta^{C=O}{}_{C_6H_{10}O}$) is plotted against the heteroatom β effect in the pentamethylene heterocycles (**3**) relative to cyclohexane ($\delta^{\beta}{}_{C_5H_{10}X} - \delta_{C_6H_{12}}$) (Figure 3), clustering occurs about a possible linear relationship ($Y = 2.04X - 3.99$ ($r = 0.769$)) in a manner reminiscent of the graph obtained for the carbonyl carbon in **1** (Figure 5 of ref 3 with $Y = 1.238X - 0.450$ ($r = 0.834$)). However, in the 1-hetera-3-cyclohexanone series, Figure 3 clearly indicates that the thia analogue **2a** does not fall on any reasonable line ($Y = 3.312X - 1.078$ ($r = 0.964$) when **2a** is omitted).

Comparison of the carbonyl chemical shifts in **2** with those in the 1-hetera-4-cyclohexanones (**1**) is shown in Figure 4. Here a reasonable linear relationship is observed for all of the heteroatom groups except the sulfone group ($Y = 1.491X -$

Table II. Infrared and Ultraviolet Absorptions of 1-Hetera-3-cyclohexanones (2)

compd	X	IR (CO),[a] cm^{-1}	λ_{max},[b] nm
cyclohexanone	CH_2	1710	285 (ϵ 14) (in hexane)
2a	S	1710 [lit. 1710, 1721 (hexane)]	251 (log ϵ 2.44), 308 (2.36) [lit. 247 (log ϵ 2.47), 305 (2.38)]
2b	$NC(=O)CH_3$	lit. 1726	
2c	$NC(=O)OCH_3$	lit. 1722, 1710	
	$NC(=O)OCH_2CH_3$	lit. 1730, 1705	
	$NC(=O)OCH_2C_6H_5$	lit. 1720, 1703	
2d	SO_2	1725	289 (log ϵ 1.37)
2e	$NCH_2C_6H_5$	1723 (lit. 1720)	280 (sh)
2f	NCH_3	1725 (lit. 1720)	288 (log ϵ 1.27)
2g	O	1725	298 (log ϵ 1.21) [lit. 298 (ϵ 6) (in MeOH)]
2h	$NC(=O)C_6H_5$	1730	

[a] As a film unless otherwise indicated. [b] In 95% ethanol unless otherwise indicated.

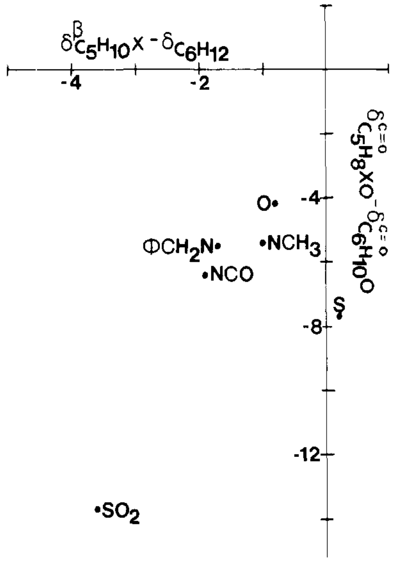


Figure 3. Comparison of the chemical shifts of the carbons β to the heteroatom in 3 (relative to cyclohexane) with the chemical shifts of the carbonyl carbons in 2 (relative to the carbonyl in cyclohexanone).

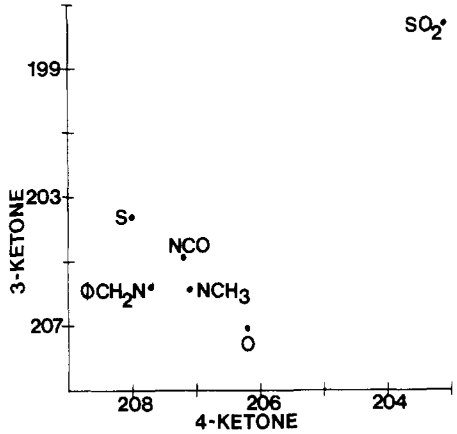


Figure 4. Comparison of the carbonyl carbon chemical shifts in 1 and 2.

103.8 (r = 0.786) for all, but $Y = -1.587X + 534.28$ (r = -0.838) without the sulfone). While neither of these correlation coefficients are satisfactory, there is some justification for considering the sulfone to be anomalous in Figure 4. In the 1-hetera-3-cyclohexanones, the sulfone (**2d**) is the only compound containing two substituents on the heteroatom. This produces a γ effect in **2d**, but a quite different δ effect in **1d**. This γ effect cancels in Figure 3, but not in Figure 4. Other than the sulfones (**1d** and **2d**), the heteroatom group with the highest carbonyl δ value in **1** has the lowest carbonyl δ value in **2**, an inverse relationship. Bearing in mind that heteroatom groups are considered (and not isolated heteroatoms), the order of the carbonyl δs (other than for the sulfone group) reflects group electronegativities, as observed for the α carbons. The most electronegative group, the oxygen, has the least effect on the β carbonyl (in **2**), in the order and direction suggested by Lambert.[5] However, the most electronegative group has the greatest effect on the γ carbonyl (in **1**), which is opposite to Lambert's analysis.[5]

The observation that the thia compound is anomalous in Figure 3 but fits the trend in Figure 4 promoted reexamination of our analysis of the behavior of 1-thia-4-cyclohexanone (**1a**) in the γ plot, Figure 5 of ref 3. Indeed this thia system deviates significantly from a linear relationship derived by omitting this point from our previous analysis ($Y = 1.524X + 0.8688$ (r = 0.870)). Without doubt, the sulfur group interacts differently with a carbonyl group from the way that any other heteroatom group[28] interacts with the carbonyl group in both systems **1** and **2**.

While increased interaction between chromophores arranged as in **2** has been suggested based on mass spectral behavior[10] and from photoelectron, ultraviolet, infrared, and proton magnetic resonance spectroscopic measurements[11-14] on selected representatives, none of these results has provided information as easily quantifiable as our ^{13}C NMR method. The unique role of sulfur in series **2** is apparent in the infrared and ultraviolet spectra (Table II) as well as in Figure 3. The ultraviolet absorptions found for **2a** were also found recently in 7-thiabicyclo[2.2.1]heptan-2-one,[29] where the 300-nm band was assigned as n,π^* and the 260-nm band with enhanced absorption was assigned as intramolecular charge transfer, as suggested herein. Photoelectron spectroscopy results using acyclic analogues[12] clearly indicate that the presence of both a sulfur and a carbonyl oxygen lone pair leads to significant stabilization of both lone pairs with respect to the monofunctional components, while the oxygen analogues show only slight stabilization of the carbonyl oxygen lone pair along with significant stabilization of the ether lone pair. In line with these stabilization arguments[15] is the fact that replacement of the β-methylene in cyclopentanone[12] by oxygen affects the basicity much less than replacement by sulfur. Whether this "sulfur effect" is unique to sulfur or typical of a second-row heteroatom requires further experimentation. Epiotis' analysis[16] of heteroatom π-donating ability may be relevant. His group[16] suggests that the π-donating ability of second-row heteroatoms is greater than that of first-row heteroatoms if the acceptor contains a low-lying LUMO and the reverse if the acceptor contains a high-lying LUMO. If the carbonyl group

Table III. Infrared and Ultraviolet Absorptions of 1-Hetera-4-cyclohexanones (1)

compd	X	registry no.	IR (C=O),[a] cm^{-1}	λ_{max},[b] nm
cyclohexanone	CH_2	108-94-1	1710 [lit. 1717 (CCl_4)]	285 (ϵ 14) (in hexane)
1a	S	1072-72-6	1715 (CCl_4) [lit. 1715 (CCl_4)]	lit. 236 (ϵ 285), 298 (33)
1b	$NC(=O)CH_3$	32161-06-1	lit. 1712 ($CHCl_3$)	
1c	$NC(=O)OCH_3$	29976-54-3	lit. broad 1700 ($CHCl_3$)	
1d	SO_2	17396-35-9	1710 (Nujol)	
1f	NCH_3	1445-73-4	1724 (CCl_4)[c] (lit. 1710)	250 (ϵ 57) [lit. 285 (ϵ 15), 293 (15) (in hexane)]
1g	O	29943-42-8	1725 (CCl_4)[c] (lit. 1718)	230 (ϵ 334)
1h	$NC(=O)C_6H_5$	24686-78-0	lit. 1722 ($CHCl_3$)	

[a] As a film unless otherwise indicated. [b] In 95% ethanol unless otherwise indicated. [c] J. Reisse, private communication.

is placed in the first category, our data[28] support Epiotis' suggestions.

Since we are now suggesting that the sulfur and carbonyl groups do interact significantly in the 1-hetera-4-cyclohexanone series (**1**) and that this interaction is apparent in the 1-hetera-3-cyclohexanone series (**2**) from infrared, ultraviolet, and ^{13}C NMR data, it behooves us to tabulate infrared and ultraviolet data for representatives of series **1**. As shown in Table III, the sulfur analogue **1a** does show a slight bathochromic shift of the longest wavelength adsorption, but solvent changes must also be recognized. The infrared absorption data do not show any pattern here.

Experimental Section

All ^{13}C NMR spectra were recorded on a JEOL PS-100 NMR spectrometer equipped with a JEOL-JNM-PFT-100 pulse unit and a JEOL-JEC-6 computer. Field frequency stabilization was established by the deuterium signal of the solvent utilized ($CDCl_3$ or $(CD_3)_2SO$). The chemical shifts are expressed in parts per million relative to internal Me_4Si at 26 ± 2 °C (unless otherwise indicated) and are believed to be accurate to 0.2 ppm. All solutions are 10–15%, so dilution effects should be minor. The spectra were obtained under conditions of proton noise decoupling, with off-resonance decoupling used to verify peak assignments where needed.

All infrared spectra were obtained with a Perkin-Elmer Model 567 grating infrared spectrometer and were run as neat liquids unless otherwise stated. Ultraviolet spectra were determined on a Beckman Acta CIII UV-vis spectrophotometer in 95% ethanol unless otherwise stated. Proton NMR spectra (^1H NMR) were recorded on a Varian Associates Model T-60A spectrometer, and chemical shifts are reported in parts per million (ppm) downfield from internal Me_4Si at ambient temperatures. Elemental analyses were performed by Alfred Bernhardt Microanalytisches Laboratorium, Elbach, W. Ger. Gas chromatographic analyses were performed on a Varian Model 3700 chromatograph fitted with a thermal conductivity detector utilizing helium flow through a 6 ft × 0.25 in 20% DEGS column on 60–80 mesh Chromosorb W.

Samples of amide **2b** and urethanes **2c** (R′ = CH_3, CH_2CH_3, and $CH_2C_6H_5$) were kindly provided by Dr. Krogsgaard-Larsen.[17]

Thian-3-one (2a). Various reported routes[18–21] using Dieckmann condensations were utilized without developing a preference for a given procedure. Literature yields and physical properties were reproduced. Product **2a** exhibited the following: bp 79–80 °C (4mm); IR 1710 cm^{-1}: ^1H NMR ($CDCl_3$) δ 3.23 (2 H, s), 3.00–2.65 (2 H, m), 2.65–2.25 (4 H, m). Anal. Calcd for C_5H_8OS: C, 51.68; H, 6.94; S, 27.60. Found: C, 51.57; H, 6.94; S, 27.80. Attempts to oxidize commercially available thian-3-ol (Aldrich Chemical Co.) using a variety of oxidants failed.

Thian-3-one 1,1-Dioxide (2d). Peroxide oxidation[19] of **2a** was performed, but yields were improved using a slightly different procedure.[22] To a solution of 1.00 g (8.62 mmol) of **2a** in 20 mL of glacial acetic acid was added 4.0 mL (40 mmol) of 30% hydrogen peroxide dropwise while maintaining the temperature at 5–10 °C. After the mixture was stirred for an additional 24 h at room temperature, the solvent was evaporated under a slow stream of nitrogen to give a white solid. Recrystallization twice from absolute ethanol afforded 0.74g (58%) of colorless flakes: mp 142–143 °C (lit.[19] mp 136–139 °C); IR (Me_2SO) 1920 and 1725 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 4.33 (2 H, s), 3.80–3.25 (2 H, m), 2.80–2.35 (2 H, m), 2.35–1.80 (2 H, m). Anal. Calcd for $C_5H_8O_3S$: C, 40.53, H, 5.45; S, 21.64. Found: C, 40.41; H, 5.46; S, 21.60.

1-Benzylazan-3-one (2e). Sodium bicarbonate treatment of the commercially available (Aldrich Chemical Co.) hydrated hydrochloride salt by the procedure of Krogsgaard-Larsen[17] smoothly provided the desired *N*-benzyl ketone in 79% yield with spectral properties as reported:[17] bp 139–140 °C (3.5 mm); IR 3030 and 1723 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.34 (5 H, s), 3.58 (2 H, s), 3.00 (2 H, s), 2.61 (2 H, t), 2.50–2.13 (2 H, m), 2.13–1.64 (2 H, m). Anal. Calcd for $C_{12}H_{15}NO$: C, 76.14; H, 8.00; N, 7.40. Found: C, 76.10; H, 7.92; N, 7.28.

1-Methylazan-3-one (2f). Jones oxidation[10] gave poor yields of product which could not be purified other than by preparative vapor-phase chromatography. Use of Jones reagent in glacial acetic acid[23] was more successful. To a solution of 3.34 g (29 mmol) of 1-methylazan-3-ol in 58 mL of glacial acetic acid was added 1.6 mL of concentrated H_2SO_4 (in one portion) followed by 11 mL of Jones reagent over a period of 20 min. After stirring for 1 additional hour, 10 mL of 2-propanol was added. Dilution with 150 mL of water was followed by addition of 25.3 g (86 mmol) of trisodium citrate and 400 mg of amalgamated zinc. The flask was flushed with N_2 for 20 min, at which time the solution was made strongly basic with 25% aqueous NaOH and extracted with methylene chloride. The organic extracts were diluted with hexane, washed with saturated aqueous NaCl, and dried (Na_2SO_4). Solvents were removed on a rotary evaporator, and the orange-brown residue was distilled under N_2 to give 1.6 g (49%) of a colorless oil which rapidly turned yellow on exposure to air: bp 68–69 °C (12.5 mm) [lit.[26] bp 63–64 °C (13 mm)]; IR 1725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.00 (2 H, s), 2.83–2.45 (2 H, m), 2.40 (3 H, s), 2.40–1.60 (4 H, m). Anal. Calcd for $C_6H_{11}NO$: C, 63.67; H, 9.82; N, 12.38. Found: 63.42; H, 9.72; N, 12.21.

Oxan-3-one (2g). Difficulties were encountered in preparation and purification by literature methods,[10,24,25] so the following sequence was developed. Hydroboration of 2,3-dihydropyran was performed using the procedure of Monson[27] with external borane generation, but with only a 5% excess of diborane. Alkaline peroxide oxidation[27] converted 8.41 g (100 mmol) of 2,3-dihydropyran into 7.52 g (74% yield) of oxan-3-ol as a colorless oil, bp 44–45 °C (0.9 mm). Jones oxidation[24] of this alcohol produced the ketone, bp 57–58 °C (9 mm), which required further purification. Column chromatography (Woelm neutral alumina I, 5:1 methylene chloride–ethyl acetate) and subsequent bulb-to-bulb distillation (Kugelrohr apparatus) produced 1.5 g (75% yield) of a colorless oil: IR 1725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.02 (2 H, s), 3.90 (2 H, t), 2.72–2.40 (2 H, m), 2.32–1.82 (2 H, m). Anal. Calcd for $C_5H_8O_2$: C, 60.05; H, 7.99. Found: C, 59.84; H, 7.91.

1-Benzoylazan-3-one (2h). Jones oxidation[30] of 1-benzoyl-3-hydroxypiperidine[30] followed by column chromatography (Woelm neutral alumina I, 3:1 chloroform–ethyl acetate) produced a 56% yield of a viscous yellow oil: IR 1730 and 1635 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.45 (5 H, s), 4.15 (2 H, s), 3.70 (2 H, t), 2.23–1.65 (2 H, m).

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Registry No.—1-Methlyazan-3-ol, 3554-74-3; 2,3-dihydropyran, 110-87-2; oxan-3-ol, 19752-84-2; 1-benzoyl-3-hydroxypiperidine, 67452-86-2.

References and Notes

(1) (a) Presented in part at the 175th National Meeting of the American Chemical Society, Anaheim, Calif. March 16, 1976, No. ORGN 158. (b) Dedicated to Professor Egbert Havinga of the University of Leiden on the occasion of his retirement.

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Three Isomeric 1,3-Dimethyl-5-(dihydropyran-2′-yl)-2,4-pyrimidinediones. Palladium-Catalyzed Synthesis and Spectrometric Properties[1]

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Reaction of 3,4-dihydro-2*H*-pyran with (1,3-dimethyl-2,4-pyrimidinedion-5-yl)mercury(II) acetate in the presence of 1 equiv of $Li_2Pd(OAc)_2Cl_2$ at 25 °C produced in high yield a mixture of two isomers, 1,3-dimethyl-5-(5′,6′-dihydro-2′*H*-pyran-2′-yl)-2,4-pyrimidinedione (1) and 1,3-dimethyl-5-(5′,6′-dihydro-2′*H*-pyran-6′-yl)-2,4-pyrimidinedione (2). Palladium-catalyzed [$(Ph_3P)_2Pd(OAc)_2$] reaction with 3,4-dihydro-2*H*-pyran with 1,3-dimethyl-5-iodo-2,4-pyrimidinedione at 100 °C yielded a third isomer, 1,3-dimethyl-5-(3′,4′-dihydro-2′*H*-pyran-2′-yl)-2,4-pyrimidinedione (3). The relationship between the three isomers was established by reduction of each to the same product, 1,3-dimethyl-5-(tetrahydropyran-2′-yl)-2,4-pyrimidinedione (7). Structure assignments of the three isomers based on mass and ^{1}H nuclear magnetic resonance spectra are discussed.

Reactions of cyclic enol ethers with palladium derivatives of nitrogen heterocycles[1] provide a potentially attractive synthetic route to C-nucleosides.[2,3] In preliminary investigations,[1] we have studied several reactions of enol ethers, including 3,4-dihydro-2*H*-pyran (**4**), with organopalladium reagents. In this report, we describe the preparation by this method and spectrometric properties of three isomeric 1, 3-dimethyl-5-(dihydropyran-2′-yl)-2, 4-pyrimidinediones (uracils) (**1**–**3**).

Two of the isomers, 1,3-dimethyl-5-(5′,6′-dihydro-2′*H*-pyran-2′-yl)-2,4-pyrimidinedione (**1**) and 1,3-dimethyl-5-(5′,6′-dihydro-2′*H*-pyran-6′-yl)-2,4-pyrimidinedione (**2**), result from reaction of 3,4-dihydro-2*H*-pyran (**4**) with an organopalladium reagent generated in situ by treatment of (1,3-dimethyl-2,4-pyrimidinedion-5-yl)mercury(II) acetate (**5**) with the palladium(II) salt $Li_2Pd(OAc)_2Cl_2$ in acetonitrile at room temperature during 1 day.[1] The reaction apparently involves regiospecific addition of an intermediate pyrimidinylpalladium species derived from **5** to the double bond of 3,4-dihydro-2*H*-pyran (**4**) followed by elimination of a hydridopalladium salt to yield the initial (major) product **1**. Readdition of the hydridopalladium salt to the double bond of the dihydropyranyl moiety of **1** and subsequent reelimination produced the double bond shifted minor product **2**.[1]

The third isomer, 1,3-dimethyl-5-(3′,4′-dihydro-2′*H*-pyran-2′-yl)-2,4-pyrimidinedione (**3**), was produced as the sole isolable product of reaction of 3,4-dihydro-2*H*-pyran (**4**) with