to 0 °C, DCC (17.9 mg, 86.9 μmol) was added, and the mixture was stirred at 0 °C for 1 h. The DCU formed was removed by filtration and the filtrates were evaporated to dryness. The oily residue was redissolved in THF (1.40 mL) and cooled to 0 °C under N_2, and DMAP (1.4 mg, 11.5 μmol) followed by **4** (21.1 mg, 78.3 μmol) was added. Ellman's test for thiols[17] was negative after 15 min at 0 °C and the mixture was poured into sodium citrate buffer pH 3.5. The product was extracted into CH_2Cl_2, and the combined organic phases were washed with 5% $NaHCO_3$ and water, dried ($MgSO_4$), and evaporated. The moist solid residue was purified by preparative layer chromatography to afford **6b** as clear oil (45.0 mg, 95%): IR ($CHCl_3$) ν_{max} 2942, 1719, 1680, 1505, 1205 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.18 (6 H, s, Bpoc *i*-Pr), 1.82–1.88 (1 H, m, β-CH_2), 1.92–1.98 (1 H, m, β-CH_2), 2.47 (1 H, t, J = 7 Hz, α-CH_2), 2.63 (1 H, t, J = 7 Hz, α-CH_2), 2.80 (1.5 H, s, NCH_3), 2.95 (1.5 H, s, NCH_3), 3.24–3.34 (4 H, m), 3.72 (3 H, s, Cys OMe), 4.56–4.62 (1 H, m, Cys CH), 5.10 (2 H, s, Cys, Bzl), 5.62–5.70 (1 H, m, Cys NH), 7.28–7.44 (10 H, m), 7.53–7.61 (4 H, m); FD mass spectrum m/e 606 (M^+).

4-[[*N*-(*tert*-Butyloxycarbonyl)-*N*-methyl-γ-aminobutyryl]thio]dibenzofuran (5a): IR ($CDCl_3$) ν_{max} 2975, 2930, 1690, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.47 (9 H, s, Boc), 1.94–2.02 (2 H, m, β-CH_2), 2.78 (2 H, t, J = 8 Hz, α-CH_2), 2.86 (3 H, s, NCH_3), 3.31 (2 H, t, J = 7 Hz, γ-CH_2), 7.32 –7.40 (2 H, m), 7.44–7.51 (2 H, m), 7.58 (1 H, d, J = 8 Hz), 7.93 (1 H, d, J = 8 Hz), 8.00 (1 H, d, J = 8 Hz); FD mass spectrum, m/e 399 (M^+).

4-[[*N*-[[(*p*-Biphenylyl)isopropyloxy]carbonyl]-*N*-methyl-γ-aminobutyryl]thio]dibenzofuran (5b): IR ($CHCl_3$) ν_{max} 2935, 1698, 1690, 1448, 1395, 1182 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.82 (6 H, s, Bpoc *i*-Pr), 1.88–1.96 (1 H, m, β-CH_2), 2.01–2.09 (1 H, m, β-CH_2), 2.72 (1 H, t, J = 7 Hz, α-CH_2), 2.82 (1 H, t, J = 7 Hz, α-CH_2), 2.86 (1.5 H, s, NCH_3), 3.01 (1.5 H, s, NCH_3), 3.30 (1 H, t, J = 8 Hz, γ-CH_2), 3.45 (1 H, t, J = 8 Hz, γ-CH_2), 7.30–7.48 (9 H, m), 7.55–7.63 (5 H, m), 7.93 (1 H, dd, J = 8, 0.5 Hz), 8.00 (1 H, dd, J = 8, 0.5 Hz); FD mass spectrum, m/e 537 (M^+).

Methyl N^{α}-(benzyloxycarbonyl)[[*N*-(*tert*-butyloxycarbonyl)-*N*-methyl-γ-aminobutyryl]thio]-L-cysteinate (6a): IR ($CHCl_3$) ν_{max} 3005, 1720, 1685, 1505, 1200 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.44 (9 H, s, Boc), 1.18–1.86 (2 H, m, β-CH_2), 2.55 (2 H, t, J = 7 Hz, γ-CH_2), 2.80 (3 H, s, NCH_3), 3..25 (2 H, b, α-CH_2), 3.32 (1 H, dd, J = 15, 6 Hz, Cys CH_2), 3.46 (1 H, dd, J = 15, 6 Hz, Cys CH_2), 3.75 (3 H, s, Cys OMe), 4.58–4.63 (1 H, m, Cys CH), 5.11 (2 H, s, Bzl), 5.75 (1 H, bd, NH), 7.34 (5 H, s, phenyl); FD mass spectrum, m/e 468 (M^+).

Representative Procedure for Deprotection. To **6b** (42.5 mg, 70.1 μmol) were added 1.5% CF_3CO_2H in CH_2Cl_2 (1.00 mL) and anisole (10 μl, 92.0 μmol). The solution was stirred at 0 °C under N_2 for 20 min and then diluted with MeOH (1.00 mL). $NaHCO_3$ (156 mg, 1.86 mmol) was added, the white suspension was stirred at 0 °C for 30 min and then diluted with water and CH_2Cl_2. The layers were separated, the aqueous phase was extracted with CH_2Cl_2, and the organic layers were combined, dried ($MgSO_4$), and evaporated. To the oily residue was added I_2 (71 mg, 279 μmol) in MeOH (2.0 mL) and the solution was stirred at 25 °C for 10 min. The mixture was then poured into chilled 5% ascorbic acid and extracted with CH_2Cl_2, and the combined organic layers were washed with water, dried ($MgSO_4$), and evaporated. The residue was purified by preparative layer chromatography to afford a viscous oil (17.3 mg, 92%) which was identical with authentic N^{α},$N^{\alpha'}$-bis(benzyloxycarbonyl)-L-cystine dimethyl ester[16] by TLC, HPLC, and ^1H NMR.

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Registry No. 1, 1119-48-8; **2a**, 94994-39-5; **2b**, 94994-40-8; **2b**·DCHA, 94994-41-9; **3**, 94994-42-0; **4**, 53907-28-1; **5a**, 94994-43-1; **5b**, 94994-44-2; **6a**, 95018-02-3; **6b**, 95018-03-4; Boc_2O, 24424-99-5; NMP, 872-50-4; 2-*p*-biphenylyl-2-propyl phenyl carbonate, 18701-36-5; N^{α},$N^{\alpha'}$-bis(benzyloxycarbonyl)-L-cystine dimethyl ester, 6968-11-2.

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Equilibrium Studies of Water and 3-Mercaptopropanoic Acid Addition to Cyclic Ketones[1]

Theodore J. Burkey and Robert C. Fahey*

Department of Chemistry, University of California, San Diego, La Jolla, California 92093

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In an earlier study we determined equilibrium constants for addition of thiols to α,β-unsaturated carbonyl groups of the type found in the A ring of steroids and concluded that their reactivity is sufficient to be of potential importance in steroid–protein interactions.[2] A study of thiol addition to methyl ketones suggested that these may also be potential sites of reaction with protein thiol groups when steric and electronic factors in the ketone are favorable.[3] Since keto groups are common substituents in rings of biologically active molecules, it is important to assess the effect of ring size on reactivity of ketones with thiols. We report here equilibrium constants for addition of 3-mercaptopropanoic acid to various cyclic ketones. In aqueous media water addition competes with thiol addition and can limit the extent to which a ketone reacts with the thiol. Where possible, equilibrium constants for water addition were also determined.

Results

Most determinations were made with 3-mercaptopropanoic acid-d_2 (3-MPA-d_2) in D_2O by ^1H NMR. Formation of hemithioketal could usually be monitored on the basis of the α-methylene proton resonance which occurred ~0.7 ppm upfield of the corresponding ketone resonance. In some cases this resonance was obscured by the β- and γ-methylene resonances of the ketone, in which case the β- or γ-methylene resonance of the hemithioketal, shifted 0.2–0.3 ppm upfield from the corresponding ketone signals, was used. Formation of 1,1-diol in water was measured by using the analogous resonances of the diol. The assignment of resonances to hemithioketal or diol was tested by showing: (1) that the signals were absent when the ketone or second reactant (3-MPA or water) was measured separately, (2) that the area of the signal for each adduct was directly dependent upon thiol or water concentration and also upon the ketone concentration, and (3) that the area of the signals for each adduct decreased reversibly with an increase in temperature. Values of K_{RSH} = [hemithioketal]/([ketone][3-MPA]) and K_{D_2O} = [diol]/([ketone][D_2O]), computed from peak area ratios as described previously,[3] are given in Tables I and II, respectively. Also included in Table I are a few values for K_{RSH} determined in dioxane in an analogous fashion. The value of K_{D_2O} for cyclobutanone is listed as tentative (Table II) because the only signal attributable to the α-protons of the diol was unresolved from the downfield ^{13}C-satellite signal of the β-methylene group of cyclobutanone, and it was necessary to correct for the satellite contribution in assessing the diol concentration.

Side reactions were not observed except in the case of cyclohexanone in D_2O. After 12 days, a solution containing an initial threefold excess of 3-MPA-d_2 over cyclohexanone showed no cyclohexanone proton signals but exhibited a triplet and two multiplets at 1.74, 1.5, and 1.3 ppm in the ratio 2:2:1. Each signal appeared at the same rate and this

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Table I. Equilibrium Constants for Addition of 3-Mercaptopropanoic Acid[a] to Cyclic Ketones

ketone	[ketone], M	[3-MPA-d_2], M	n^b	K_{RSD}, M^{-1}
cyclobutanone	0.6	0.3–1.0	4	0.061 ± 0.007
	0.34	0.57	1	0.012[c,d]
	0.9–3.2	0.8–3.0	4	0.017 ± 0.005[c,e]
cyclopentanone	2.2	3.4	2	<0.002
cyclohexanone	0.095	0.29–1.15	4	0.065 ± 0.011
	1.5–2.7	1.1–1.3	2	0.020 ± 0.003[c]
	0.33–2.6	0.77–4.9	16	0.034 ± 0.012[c,e]
cycloheptanone	2.31	1.5	1	0.0025[c–e]
cyclooctanone	0.26–0.29	1.15	2	<0.001
tetrahydropyran-4-one	0.54	0.12–1.2	6	0.73 ± 0.14
4-piperidone	0.16–0.2	0.12–1.2	4	12.7 ± 2.1[f]

[a] In D_2O at 34 °C and by ^1H NMR except as noted. [b] Number of determinations. [c] K_{RSH} in dioxane. [d] Tentative value. [e] By ^{13}C NMR. [f] At pH 2.5–3.3.

Table II. Equilibrium Constants for D_2O Addition to Cyclic Ketones[a]

ketone	[ketone], M	[D_2O], M	n^b	$10^3K_{D_2O}$, M^{-1}
cyclobutanone	0.33	54	1	0.06[c]
cyclopentanone	0.11–1.1	50–55	4	<0.001
cyclohexanone	0.24–0.48	53	5	0.53 ± 0.16
cyclooctanone	0.291	53	3	<0.02
tetrahydropyran-4-one	0.54	42–53	7	4.5 ± 0.5
4-piperidone	0.16–0.2	48–52	6	102 ± 7[d]

[a] In D_2O at 34 °C and by ^1H NMR. [b] Number of determinations. [c] Tentative value. [d] At pH 2.5–3.3.

corresponded to the rate of disappearance of the signals due to cyclohexanone plus its hemithioketal. These observations, plus the fact that the thioketal from 2-mercaptoethanol and cyclohexanone is known to form under similar conditions,[4] suggest that this side reaction involves thioketal formation.

The complexity of the ^1H NMR spectra for larger ketones prompted us to explore ^{13}C NMR as an alternative method for measurement of K_{RSH} in dioxane. The difficulty with conventional ^{13}C NMR (broad-band proton decoupling, short delay times, and small flip angles) is that variable NOE's (nuclear Overhauser effects) and unequal saturation of signals resulting from different T_1's (spin–lattice relaxation times) can result in peak area ratios for two substances that differ significantly from their molar ratios. As pointed out by Mareci and Scott[5] this problem can be minimized if the ratios are derived from measurements of carbons having similar NOE's and T_1's, i.e., carbons in very similar environments. In the present system this is most nearly achieved by using the carboxyl group of 3-MPA and the corresponding group of the hemithioketal (shifted 0.5 ppm downfield from 3-MPA) to assess the thiol:hemithioketal ratio. This approach gave a value for K_{RSD} with fluoroacetone which was 10% greater than that found by ^1H NMR.[6] With cyclobutanone and cyclohexanone (Table I) the ^{13}C NMR method gave values 40% and 70% greater than those measured by ^1H NMR. This likely reflects a decrease in T_1 for the hemithioketal relative to 3-MPA-d_2 resulting in a corresponding increase in its relative signal intensity. The result is an overestimation of the hemithioketoal to thiol ratio and therefore of the value of K_{RSH}. It proved impractical to study addition to cycloheptanone by ^1H NMR. The value obtained by ^{13}C NMR (Table I) is likely to be high, perhaps by as much as a factor of 2, on the basis of the above considerations.

Discussion

The values of K_{RSH} and K_{D_2O} found for cyclohexanone (Tables I and II) are 10–20 times greater than those found previously for acetone[3] and the variation of K_{RSD} and K_{D_2O} with ring size follows the pattern $C_4 > C_5 < C_6 > C_7 > C_8$. These variations with structure are analogous to those found for other reactions involving conversion of an sp^2 to an sp^3 hybridized carbon and have been attributed to the effects of ring size upon bond angle distortion and upon eclipsing of vicinal bonds.[7,8] The large equilibrium constants for tetrahydropyran-4-one and 4-piperidone hydrochloride, relative to cyclohexanone, result from the relief of unfavorable dipole–dipole and charge–dipole interactions in the ketone upon formation of the hemithioketal and are analogous to the electronic effects found in methyl ketones.[3] A value of 5.0 was reported for the diol:ketone ratio with 4-piperidone in 2 M phosphate buffer (pH 6–7, 32 °C)[9] which yields a value of $K_{H_2O} = 0.10$, assuming a water concentration of 50 M. Since isotope effects appear to be small for this reaction,[3] this result is in accord with the value for K_{D_2O} given in Table II.

The potential biological importance of hemithioketal formation involving cyclic ketones can be assessed on the basis of the rationale outlined previously.[2,3] We consider first the reaction with glutathione (GSH), a thiol found in most eucaryotic cells at 1–10 mM concentrations. The value of K_{RSH} must be greater than 10 M^{-1} and the ratio K_{RSH}/K_{H_2O} must be greater than 500 for 10% or more of the ketone to form hemithioketal.[3] If 3-MPA is used as a model for glutathione, the results of Tables I and II show that none of the cyclic ketones studied meet these criteria. Thus, reaction of cyclic ketones with GSH to form hemithioketals is not expected to be a favorable process in cells.

The possibility also exists that cyclic ketones can react with protein thiol groups, providing certain conditions are met.[3] If the cyclic ketone binds with low affinity to a protein having a favorably positioned thiol group, then thiol addition to the ketone can occur in a fashion analogous to an intramolecular process. This will be much more favorable than the intermolecular reactions measured by K_{RSD} and the predicted ratio of intra- to intermolecular equilibrium constants could be a factor of $\sim 10^6$ M.[3,10] It follows that for cyclic ketones having intermolecular K_{RSH} values > 0.01 M^{-1} the formation of a thiohemiketal by reaction between a protein thiol group and a bound ketone functionality could make a difference of $\sim 10^4$ in the binding of the small molecule to the protein, thus converting a low affinity binding to a high affinity binding.

Experimental Section

Materials. All ketones were from Aldrich and were used without further purification, except cyclohexanone which was

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prepared from its bisulfite adduct,[11] distilled, and purified further by preparative GC (4 ft × 1/4 in. 10% SE 52 in series with 8 ft × 1/4 in. 20% DEGS on Chromosorb P). Preparation of all other reagents was as previously described.[3] Base-catalyzed reaction conditions were used to minimize thioketal formation, and sample preparation for ^{13}C NMR was similar to that for ^{1}H NMR.[3] Typically, an aliquot of neat 3-MPA (0.04 mL, 4.6 mmol) was added to a 10-mm NMR tube containing anhydrous K_2CO_3 (13 mg, 90 μmol). After bubbling subsided, dioxane (0.9 mL) and cyclobutanone (0.2 mL, 2.7 mmol) were added. A 5-mm reference tube containing D_2O for the NMR field lock was held coaxially in the NMR tube by a Teflon-brand sleeve.

NMR Spectra. ^{1}H NMR spectra were recorded on an EM 390 90-MHz CW spectrometer or a 360-MHz Ft spectrometer interfaced to a Nicolet computer. Pulse widths were routinely 5 μs (90°), acquisition times were 4 s, and delay times were 1 s. Redfield 2-1-4 and soft pulse sequences were used in a few cases where small signals were measured in the presence of large ones.[12] For the pulse lengths used, the effective field of the carrier pulse decreases significantly after a few hundred hertz. By placing the carrier frequency midway between two signals to be measured, the difference in the effective field of the two signals was minimized. Measurements were made as soon as the addition reaction came to equilibrium. Routine conditions were used for acquiring ^{13}C spectra (20° flip angle, 0.6 s acquisition time, and 1 s delay time).

Registry No. D_2O, 7789-20-0; 3-MPA-d_2, 95193-08-1; cyclobutanone, 1191-95-3; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; cycloheptanone, 502-42-1; cyclooctanone, 502-49-8; tetrahydropyran-4-one, 29943-42-8; 4-piperidone, 41661-47-6.

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Gallium Trichloride and Superacid-Catalyzed Isomerization of Mixed Hexaalkylbenzenes and NMR Spectroscopic Study of the Intermediate Hexaalkylbenzenium Ions and Related Hexa- and Heptaalkylbenzenium Ions[1]

George A. Olah,* Khosrow Laali, George Adler, Robert J. Spear, Richard Schlosberg, and Judith A. Olah

Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, University Park, Los Angeles, California 90089, and Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

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A substantial number of methyl-substituted benzenium ions ranging from methylbenzenium ion to heptamethylbenzenium ion have been prepared and studied.[2] The charge distribution patterns in these ions have been discussed on the basis of their ^{1}H and ^{13}C NMR data.[2-4] Both the X-ray structure[5] and CPMAS ^{13}C NMR[6,7] spectrum of isolated crystalline heptamethylbenzenium tetrachloroaluminate were reported. Ethyl-substituted benzenium ions including the heptaethylbenzenium ion were also reported. The heptaethylbenzenium ion was identified in the "red-oil" complex layers which are formed during the $AlCl_3$-catalyzed ethylation of benzene with ethylene.[8]

We now report the Friedel-Crafts isomerization of a series of mixed hexaalkylbenzenes, namely, isomeric diethyltetramethylbenzenes and dineopentyltetramethylbenzenes. We also studied their intermediate protonated hexaalkylbenzenium ions in FSO_3H-SbF_5 (4:1)/SO_2 and HF-SbF_5 (1:1)/SO_2ClF solution at -20 to -70 °C. Protonation of hexaisopropylbenzene in FSO_3H-SbF_5 (1:1)/SO_2ClF has also been carried out. Further we have also generated and studied by ^{13}C NMR spectroscopy a series of related heptaalkylbenzenium ions formed by low-temperature ipso alkylation of hexamethyl- and hexaethylbenzene with Me_2C^+H and Me_3C^+ generated in SbF_5/SO_2ClF solution.

Table I. $GaCl_3$-Catalyzed Isomerization of Hexaalkylbenzenes in Freon-113 Solution at 30 °C[a]

hexaalkylbenzene	isomer distribution (%) ortho	meta	para
o-$(C_2H_5)_2(CH_3)_4C_6$ (1)	32.4	40.5	27.1
m-$(C_2H_5)_2(CH_3)_4C_6$ (2)	35.5	41.0	23.5
p-$(C_2H_5)_2(CH_3)_4C_6$ (3)	37.6	44.6	17.8
o-$[CH_2C(CH_3)_3]_2(CH_3)_4C_6$ (4)	41.5	31.8	26.7
m-$[CH_2C(CH_3)_3]_2(CH_3)_4C_6$ (5)	31.4	34.2	34.4
p-$[CH_2C(CH_3)_3]_2(CH_3)_4C_6$ (6)	21.8	29.2	49.0

[a] Average reaction time was 16 hs.

Results and Discussion

When hexaethylbenzene was treated with $AlCl_3$ in benzene solvent at 30 °C for 1 h no dealkylation or transalkylation was observed. Similarly treatment of isomeric diethyltetramethylbenzenes 1-3 with SbF_5 in 1,1,2-trifluorotrichloroethane (Freon-113) solution at 30 °C overnight gave no evidence of isomerization.

Addition of a proton source to the Lewis acid, however, promotes isomerization. Thus in our studies of Friedel-Crafts isomerization of hexaalkylbenzenes 1-6 we have found that $GaCl_3$ in Freon-113 as solvent and in the presence of a trace of water to provide a proton source is an efficient isomerization catalyst. No byproduct could be detected in these reactions. The results obtained are summarized in Table I.

When same isomeric 1-6 were dissolved in FSO_3H-SbF_5 (4:1)/SO_2 solution at -20 °C the ^{1}H NMR spectra of the resulting benzenium ions in all cases indicated formation and ready interchange of both possible, energetically similar, benzenium ions resulting from protonation ipso to methyl as well as ethyl groups. For example in case of 3

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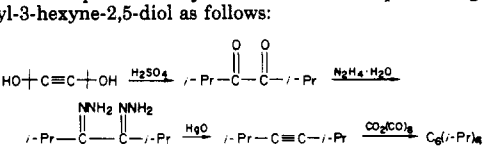

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