The Enol-Enethiol Tautomerism of Simple Nonaromatic β-Thioxo Ketones. An Approach to Quantitative Description Based upon ^{1}H NMR and UV Spectral Parameters and the Adaptation of These into a Simplified Model of the Tautomeric Equilibrium[1]

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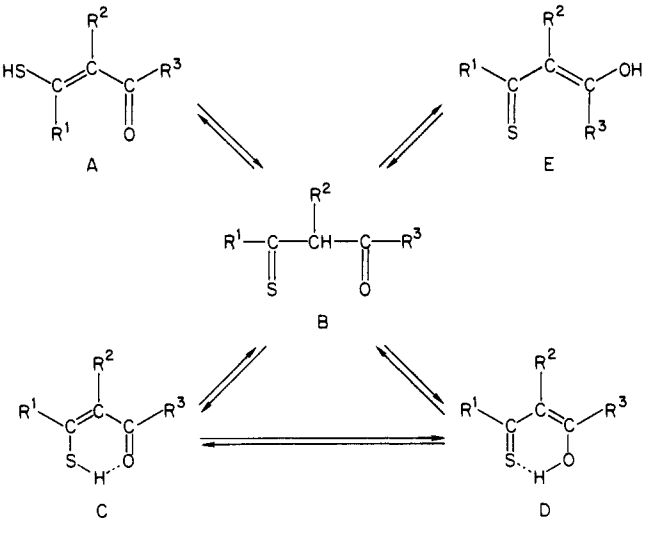
Abstract: The ^{1}H NMR and UV spectra of 31 aliphatic and alicyclic β-thioxo ketones have been measured in various solvents (cyclohexane, CCl_4, dioxane, CH_2Cl_2, $CHCl_3$, and MeCN—^{1}H NMR spectra in corresponding perdeuterated solvents). The spectra have been interpreted in terms of the general coexistence of two rapidly interconverting tautomeric forms, the intramolecularly hydrogen-bonded (*Z*)-enol and (*Z*)-enethiol forms, respectively, the interconversion taking place by chelate–proton transfer. UV absorbance ratios A_D/A_C (A_D and A_C refer to the absorbances of $\pi \rightarrow \pi^*$ transition of the enolic O—C=C—C=S and the enethiolic O=C—C=C—S chromophoric systems, respectively) and weigted average ^{1}H NMR chelate–proton chemical shifts have been correlated by adaptation to a model idealizing the (*Z*)-enol/(*Z*)-enethiol equilibrium as an entity in itself, the flanking groups R^1 and R^3 playing parts as regulators of the site of the equilibrium. Computations based on this model, besides indicating the significance of the solvent as equilibrium regulator, lead to determination of the site of the equilibrium (in terms of the mole fraction x_D of the enolic constituent) at ambient temperature for every single β-thioxo ketone in any of the six solvents. The site of the (*Z*)-enol/(*Z*)-enethiol equilibrium system is governed principally by intramolecular factors (i.e., the nature of R^1, R^2, and R^3) and secondarily by extramolecular factors (nature of the solvent). Usually, the (*Z*)-enol form, possessing strong intramolecular hydrogen bonding, predominates over the (*Z*)-enethiol form, in which the intramolecular hydrogen bonding appears to be weak and of little importance as a stabilizing factor. It is suggested that the present approach exemplifies a tool relevant for the study of similar tautomeric two-component systems characterized by rapid interconversion.

During the last 15 years β-thioxo ketones[2,3] have attracted considerable attention, mainly and originally in connection with investigations of the chelating abilities and analytical applications of the more stable members of this particular class of compounds.[4,5] Although based upon a limited number of synthetic principles, quite a few procedures for the preparation of β-thioxo ketones have already been described.[1,6-22] The potentiality of using

Scheme I



β-thioxo ketones, the monosulfur-analogues of β-diketones, in the synthesis of sulfur-containing heterocyclic compounds is conspicuous and has in fact been demonstrated.[23] However, from a physicochemical point of view, β-thioxo ketones are of particular interest as model compounds for studies of prototropic tautomerism and intramolecular hydrogen chelation, not least because of the molecular asymmetry generated conveniently by the incorporation

(1) β-Thioxo ketones. Part 12. For Part 11, see: Duus, F. *Synthesis* **1985**, 672.
(2) For simplicity, the β-thioxo ketones are throughout named as such regardless of which of the possible tautomeric forms in the individual cases may be dominant.
(3) β-Thioxo ketones were reported as existing species for the first time in 1963–1964: (a) Mayer, R.; Hiller, G.; Nitzschke, M.; Jentzsch, J. *Angew. Chem.* **1963**, *75*, 1011. (b) Chaston, S. H. H.; Livingstone, S. E. *Proc. Chem. Soc.* **1964**, 111. (c) Uhlemann, E.; Klose, G.; Müller, H. *Z. Naturforsch.* **1964**, *19b*, 962. (d) Klose, G.; Müller, H.; Uhlemann, E. *Z. Naturforsch.* **1964**, *19b*, 952. The compound described in an earlier paper (Tornetta, B.; Agnello, S. *Ann. Chim. (Rome)* **1958**, *48*, 581 [*Chem. Abstr.* **1959**, *53*, 6151]) as 1,3-diphenyl-3-thioxopropan-1-one is most likely rather the disulfide derived from the enethiol tautomer of this compound (cf. ref 9).
(4) For reviews dealing mainly with the chelating properties of β-thioxo ketones, see: (a) Cox, M.; Darken, J. *Coord. Chem. Rev.* **1971**, *7*, 29. (b) Livingstone, S. E. *Ibid.* **1971**, *7*, 59. (c) Uhlemann, E.; Müller, H.; Thomas, P. *Z. Chem.* **1971**, *11*, 401. (d) Uhlemann, E.; Morgenstern, R. *Ibid.* **1977**, *17*, 405. (e) Mehrotra, R. C.; Bohra, R.; Gaur, D. P. "Metal β-Diketonates and Allied Derivatives"; Academic Press: London, 1978; Chapters 4 and 5.
(5) For a most up-to-date review, see: Duus, F. In "Comprehensive Organic Chemistry"; Barton, D. H. R. Ollis, W. D., Eds.; Jones, D. N., Volume Ed.; Pergamon Press: Oxford, 1979; Vol. 3, Chapter 11.22.
(6) Uhlemann, E.; Müller, H. *Angew. Chem.* **1965**, *77*, 172.
(7) Uhlemann, E.; Thomas, P. *Z. Chem.* **1967**, *7*, 430.
(8) Yokoyama, A.; Kawanishi, S.; Tanaka, H. *Chem. Pharm. Bull.* **1970**, *18*, 356.
(9) Carlsen, L.; Duus, F. *Synthesis* **1977**, 256.
(10) (a) Bayer, E.; Müller, H.-P. *Tetrahedron Lett.* **1971**, 553. (b) Bayer, E.; Müller, H.-P.; Sievers, R. *Anal. Chem.* **1971**, *43*, 2012.
(11) Beyer, L.; Sittel, H.; Pulst, M.; Hoyer, E. *Z. Chem.* **1974**, *14*, 469.
(12) Chaston, S. H. H.; Livingstone, S. E.; Lockyer, T. N.; Pickles, V. A.; Shannon, J. S. *Aust. J. Chem.* **1965**, *18*, 673.
(13) (a) Ho, R. K. Y.; Livingstone, S. E.; Lockyer, T. N. *Aust. J. Chem.* **1965**, *18*, 1927. (b) Ho, R. K. Y.; Livingstone, S. E.; Lockyer, T. N. *Ibid.* **1966**, *19*, 1179. (c) Ho, R. K. Y.; Livingstone, S. E.; Lockyer, T. N. *Ibid.* **1968**, *21*, 103.
(14) Belcher, R.; Stephen, W. I.; Thomson, I. J.; Uden, P. C. *J. Inorg. Nucl. Chem.* **1971**, *33*, 1851.
(15) Belcher, R.; Stephen, W. I.; Thomson, I. J.; Uden, P. C. *J. Inorg. Nucl. Chem.* **1972**, *34*, 1017.
(16) Berg, E. W.; Reed, K. P. *Anal. Chim. Acta* **1966**, *36*, 372.
(17) Duus, F.; Lawesson, S.-O. *Ark. Kemi* **1968**, *29*, 127.
(18) Joshi, K. C.; Pathak, V. N.; Kumawat, K. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1127.
(19) Duus, F.; Anthonsen, J. W. *Acta Chem. Scand., Ser. B* **1977**, *31*, 40.
(20) Duus, F. *J. Org. Chem.* **1977**, *42*, 3123.
(21) Uhlemann, E.; Thomas, P. *J. Prakt. Chem.* **1966**, *34*, 180.
(22) Uhlemann, E.; Eckelmann, U. *Z. Anorg. Allg. Chem.* **1971**, *383*, 321.
(23) Reference 5, p 396.

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of the sulfur atom. Hitherto forwarded contributions to the discussion of the structural properties of β-thioxo ketones have been based on ^{1}H NMR,[15-20,24-29] IR,[12,15-22,29-23] Raman,[19,32] UV-visible,[19-21,34-38] and photoelectron (PE)[39-41] spectroscopic studies. Three contributions depend on the application of X-ray and neutron diffractometric methods.[42-44]

Erroneous interpretations have been made, especially in the pioneering papers (ref 12, 15, 17, 24, 31, and 32). However, present evidence (particularly ref 19, 20, 25, 27, 28, 35–38, and 40–44) strongly suggests that β-thioxo ketones, under conditions of thermodynamic equilibrium in any state of macroscopic existence, in reality hardly exist as such, as long as a present α-hydrogen atom at all makes tautomeric change feasible (Scheme I). Absence of α-hydrogen atoms naturally necessitates β-thioxo ketones such as 3,3-dimethyl-4-thioxopentan-2-one[45] and 2,2,4,4-tetramethyl-3-thioxocyclobutanone[46] to exist as such, but otherwise the following picture of the tautomeric phenotype of β-thioxo ketones looms:[47]

(1) Open-chain α-unsubstituted aromatic[42,43] and apparently also nonaromatic[44] β-thioxo ketones exist in the solid crystalline state solely in the hydrogen-chelating enolic form D (Scheme I).

(2) In solution, as neat liquids, and in the gas phase, the majority of the known β-thioxo ketones possessing the appropriate structural qualifications exist exclusively as tautomeric equilibrium mixtures of rapidly interconverting protonchelating (*Z*)-enol and (*Z*)-enethiol forms (D and C, respectively, Scheme I), the interconversion taking place extremely rapidly by intramolecular proton transfer (ref 19, 20, 25, 27, 28, 35–38, 40, and 41). This finding is supported by theoretical contemplations.[35,37,38,48] β-Thioxo ketones exhibiting this structural phenotype, in the following referred to as "simple" β-thioxo ketones, comprise aromatic as well as nonaromatic open-chained α-unsubstituted β-thioxo ketones, 2-acylcycloalkanethiones, and some 2-thioacylcycloalkanones.

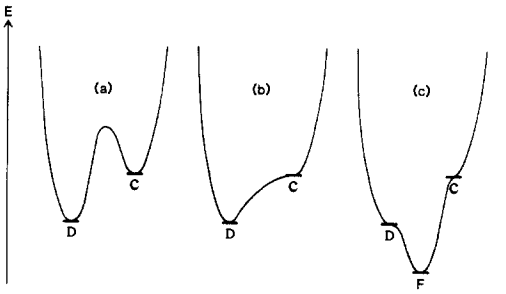


Figure 1. (a) Unsymmetrical double-minimum potential-energy function illustrating the energetics connected with the tautomeric interconversion process C ⇄ D (D is usually the relatively more stable tautomeric form). (b) Unsymmetrical single-minimum potential-energy function corresponding to a hypothetic situation implying the ground-state existence of merely one hydrogen-chelating form (D). In this case the chelate proton transfer process is degenerated to a vibrational transition. (c) Unsymmetrical single-minimum potential-energy function corresponding to the hypothetic situation implying the existence of a resonance-stabilized "pseudoaromatic" species F (in this representation C and D would represent resonance forms).

(3) β-Thioxo ketones that are substituted at the α-position and further have a freely rotating R^1–CS– moiety (i.e., R^1 and R^2 do not jointly form a cyclic system) also exist as the C ⇄ D equilibrium mixture but may, as an extension of the tautomeric equilibrium system, exist additionally in the (*E*)-enethiol form A (Scheme I).[20,49]

(4) The (*E*)-enol form E constitutes an exceptional state of existence for β-thioxo ketones and requires for population either special steric conditions[25,49] or other special intramolecular qualifications.[50]

Scheme I gives a survey over all generally possible tautomeric forms of β-thioxo ketones and the plausible pathways of interconversion. All interconversion processes except that involving simple chelate proton transfer (i.e., the C ⇄ D process) are relatively slow. Consequently, whenever (*E*)-enol (E) and (*E*)-enethiol (A) forms are constituents of a tautomeric equilibrium mixture, they are NMR spectroscopically distinguishable as individuals.[20,25]

However, "simple" β-thioxo ketones characteristically display at ordinary temperatures the ^{1}H NMR spectral pattern of merely a single species, characterized by a chelate proton signal at low field within the range δ 4–16, the actual signal position depending primarily on the nature of the β-thioxo ketone, secondarily on the nature of the solvent, and tertiarily on the temperature and the concentration of the β-thioxo ketone.[19,20,27,36] Recent dynamic ^{1}H NMR studies[28] have efficiently proved that this single species spectrum in fact is to be considered as a weighted average spectrum of those of the strongly chelated (*Z*)-enol form D and the weakly chelated (*Z*)-enethiol form C in consequence of their very rapid interconversion (on the NMR time scale); at sufficiently low temperature the constituents C and D are indeed NMR spectroscopically distinguishable as individuals.[28] Hence C and D are clearly separated by an activation energy barrier as depicted in Figure 1a,[51] and other interpretations in terms of the general existence of merely the enethiol form C,[12-17,32,33] merely the enol form D,[24] or eventually a resonance-stabilized "pseudoaromatic" species F, characterized by extensive π-electron delocalization and by having the acidic hydrogen atom localized somewhere between the chelating sulfur and oxygen atoms (the latter situation is visualized in Figure 1c),[52] are efficiently ruled out.

(24) (a) Klose, G.; Thomas, P.; Uhlemann, E.; Märki, J. *Tetrahedron* **1966**, *22*, 2695. (b) Uhlemann, E.; Thomas, P.; Klose, G.; Arnold, K. *Z. Anorg. Allg. Chem.* **1969**, *364*, 153. (c) Arnold, K.; Klose, G.; Thomas, P.; Uhlemann, E. *Tetrahedron* **1969**, *25*, 2957. (d) Arnold, K.; Klose, G. *Ibid.* **1969**, *25*, 3775.

(25) Klose, G.; Arnold, K.; Eckelmann, U.; Uhlemann, E. *Tetrahedron* **1972**, *28*, 6019.

(26) Klose, G.; Lochmann, R.; Ludwig, E.; Uhlemann, E. *J. Mol. Struct.* **1981**, *72*, 281.

(27) (a) Yusupov, I. A.; Gindin, V. A.; Ershov, B. A.; Kol'tsov, A. I. *Zh. Org. Khim.* **1978**, *14*, 210. (b) Gindin, V. A.; Pashkevich, K. I.; Nikol'skii, A. L.; Ershov, B. A.; Kol'tsov, A. I.; Yusupov, I. A.; Postovskii, I. Y. *Ibid.* **1979**, *15*, 1773.

(28) Berg, U.; Sandström, J.; Carlsen, L.; Duus, F. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1321.

(29) Kumawat, K. R. *Indian J. Chem.* **1981**, *20B*, 759.

(30) Uhlemann, E.; Thomas, P. *Z. Anorg. Allg. Chem.* **1967**, *356*, 71.

(31) Chaston, S. H. H.; Livingstone, S. E. *Aust. J. Chem.* **1967**, *20*, 1065.

(32) Sliman, O.; Fresco, J.; Gray, H. B. *J. Am. Chem. Soc.* **1974**, *96*, 2347.

(33) (a) Gebicki, J.; Krantz, A. *J. Chem. Soc., Chem. Commun.* **1981**, 486. (b) Gebicki, J.; Krantz, A. *J. Am. Chem. Soc.* **1981**, *103*, 4521.

(34) Chaston, S. H. H.; Livingstone, S. E. *Aust. J. Chem.* **1967**, *20*, 1079.

(35) Carlsen, L.; Duus, F. *J. Am. Chem. Soc.* **1978**, *100*, 281.

(36) Carlsen, L.; Duus, F. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1532.

(37) Carlsen, L.; Duus, F. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1768.

(38) Fabian, J. *Tetrahedron* **1973**, *29*, 2449.

(39) Carnovale, F.; Gan, T. H.; Peel, J. B.; Franz, K.-D. *J. Chem. Soc., Perkin Trans. 2* **1980**, 957.

(40) Jørgensen, F. S.; Carlsen, L.; Duus, F. *J. Am. Chem. Soc.* **1981**, *103*, 1350.

(41) Jørgensen, F. S.; Brown, R. S.; Carlsen, L.; Duus, F. *J. Am. Chem. Soc.* **1982**, *104*, 5922.

(42) (a) Power, L. F.; Turner, K. E.; Moore, F. H. *J. Chem. Soc., Perkin Trans. 2* **1976**, 249. (b) Preliminary communication: Power, L. F.; Turner, K. E.; Moore, F. H. *Tetrahedron Lett.* **1974**, 875.

(43) Richter, R.; Sieler, J.; Kaiser, J.; Uhlemann, E. *Acta Crystallogr., Ser. B* **1976**, *32*, 3290.

(44) Nørskov-Lauritsen, L.; Carlsen, L.; Duus, F. *J. Chem. Soc., Chem. Commun.* **1983**, 496.

(45) Burgot, J.-L.; Masson, J.; Metzner, P.; Vialle, J. *Tetrahedron Lett.* **1976**, 4297.

(46) Elam, E. U.; Davis, H. E. *J. Org. Chem.* **1967**, *32*, 1562.

(47) For recent deviant views based on studies of aromatic and polyfluorinated aromatic β-thioxo ketones, see ref 26 and 29. The interpretation forwarded recently by Gebicki and Krantz (ref 33) has proved untenable (ref 28 and 44). The existence of a thioxo ketone form (B) of 1,1,1,5,5,5-hexafluoro-4-thioxopentan-2-one (ref 10) is questioned; the reported evidences suffer from ambiguity.

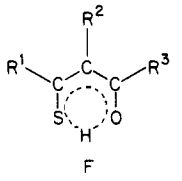
(48) Carlsen, L.; Duus, F. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1080.

(49) Duus, F., to be published.

(50) According to UV investigations thiodimedone (5,5-dimethyl-3-thioxocyclohexan-1-one) is purely enethiolic (A form) in nonpolar solvents but exists in polar solvents (ethanol and Me_2SO) as an equilibrium mixture of A and E forms: Dalgaard, L.; Lawesson, S.-O. *Acta Chem. Scand., Ser. B* **1974**, *28*, 1077.

(51) For thioacetylacetone in Freon solution, $\Delta G^{\ddagger}$ (enol D → enethiol C) was found to be 8.9 ± 0.1 kcal/mol (see ref 28).

(52) This possibility has been discussed but was not considered likely (see ref 35).



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The UV spectra of simple β-thioxo ketones are in complete accord with the existence of a mobile C ⇄ D equilibrium system,[19,20] displaying constantly two characteristic absorption bands of conversely related intensities in the regions around 290 nm ($\pi \rightarrow \pi^*$ transition within the S—C=C—C=O chromophore system of C)[19,28,36,38,53] and around 360 nm ($\pi \rightarrow \pi^*$ transition within the O—C=C—C=S chromophore system of D).[38,54,55]

For the sake of completeness it should be mentioned that the UV photoelectron,[40] the X-ray photoelectron,[41] and the IR[19,20] spectra of simple β-thioxo ketones, so far recorded, also corroborate the existence of the C ⇄ D equilibrium system.

The work described here was initiated with the intention of providing further evidence for the generality of the C ⇄ D equilibrium system as a phenotype of simple β-thioxo ketones. However, in view of the knowledge recently obtained from dynamic ^{1}H NMR studies,[28] we found it expedient to focus rather on quantitative aspects of the observed spectral characteristics, for the present particularly on the ^{1}H NMR and UV spectral observables and their correlative implications.

The Model

Assuming general existence of the C ⇄ D equilibrium system and correctness of the assignment of the observed characteristic UV absorption bands at around 290 and 360 nm as $\pi \rightarrow \pi^*$ transitions arising from the chromophore systems S—C=C—C=O and O—C=C—C=S, respectively, the intensities of these bands reflect the relative equilibrium concentrations of the tautomeric forms C and D, respectively. Hence, according to the Beer–Lamberts law,[56] we can assume validity of the equations

$$A_C = \epsilon_C c_{tot} x_C \quad (1)$$

and

$$A_D = \epsilon_D c_{tot} x_D \quad (2)$$

where A_C and A_D are the measured absorbances at λ_C (wavelength of absorption maximum of $\pi \rightarrow \pi^*$ transition of chromophore S—C=C—C=O of C) and λ_D (wavelength of absorption maximum of transition of chromophore O—C=C—C=S of D), ϵ_C and ϵ_D are the respective molar extinction coefficients, c_{tot} is the total concentration of the β-thioxo ketone (i.e., $c_{enol} + c_{enethiol}$), and x_C and $x_D = 1 - x_C$ are the respective equilibrium mole fractions of C and D. Assuming further that the substituents R^1, R^2, and R^3 do not influence band intensities decisively (except as equilibrium regulators), we may ascribe validity of eq 1 and 2 not only to the C ⇄ D equilibrium of individual simple β-thioxo ketone systems but also in a wider sense to the C ⇄ D equilibrium as such. Of course, the latter assumption implies severe restrictions as to the nature of R^1, R^2, and R^3. Most important, conjugation beyond the central chelate system cannot be allowed. This lead us to consider merely aliphatic and alicyclic simple β-thioxo ketones as suitable model compounds.

As stated above, the rapid interconversion between the tautomeric forms C and D implies the observation of weighted average ^{1}H NMR spectra. Hence, for a given β-thioxo ketone, we can assume validity of the equation[57]

$$\delta^{obsd}_{chel\text{-}H} = x_C \delta_{SH} + x_D \delta_{OH} \quad (3)$$

where $\delta^{obsd}_{chel\text{-}H}$ refers to the observed weighted average chelate proton chemical shift, x_C and $x_D = 1 - x_C$ are the equilibrium mole fractions of forms C and D, respectively, and δ_{SH} and δ_{OH} denote the nonobservable real chelate proton shifts of forms C and D, respectively. Assuming furthermore that variations in chelate proton shielding contributions depending on the nature of R^1, R^2, and R^3 can be ignored, we may ascribe validity of eq 3 to the general C ⇄ D equilibrium system (i.e., R^1, R^2, and R^3 are considered to act merely as equilibrium regulators) in otherwise unaltered surroundings. At first sight this may look like a crude approximation. However, compared with the very wide range of the observed chelate proton resonances (δ 4–16, Table I), substituent and medium contributions to $\delta^{obsd}_{chel\text{-}H}$ cannot be decisive, as long as only appropriate flanking groups R^1, R^2, and R^3 (saturated aliphatic and alicyclic systems) and aprotic solvents are considered.[58] Furthermore, from a statistical point of view, the selection of a sufficient number of variedly substituted β-thioxo ketones might enable us to control the medium shielding contribution to $\delta^{obsd}_{chel\text{-}H}$ by considering separately sets of chelate proton chemical shifts measured in different solvents.

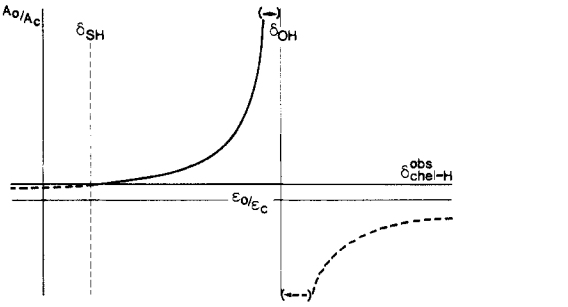


Figure 2. Graphical outline of the function $A_D/A_C = (\epsilon_D/\epsilon_C)\{(\delta^{obsd}_{chel\text{-}H} - \delta_{SH})/(\delta_{OH} - \delta^{obsd}_{chel\text{-}H})\}$ (eq 4). The physically pertinent part of the hyperbolic curve is indicated by the full-drawn line.

Combination of eq 1, 2, and 3, under the elimination of c_{tot}, x_C, and x_D, yields the equation

$$\frac{A_D}{A_C} = \frac{\epsilon_D}{\epsilon_C} \frac{\delta^{obsd}_{chel\text{-}H} - \delta_{SH}}{\delta_{OH} - \delta^{obsd}_{chel\text{-}H}} \quad (4)$$

Mathematically, eq 4 describes the observable UV absorbance ratio A_D/A_C as a hyperbolic function of the observable chemical shift $\delta^{obsd}_{chel\text{-}H}$, the hyperbola being determined by the assymptotes $\delta^{obsd}_{chel\text{-}H} = \delta_{OH}$ and $A_D/A_C = -\epsilon_D/\epsilon_C$, $\delta^{obsd}_{chel\text{-}H} = \delta_{SH}$ marking the intersection of the hyperbola with the $\delta^{obsd}_{chel\text{-}H}$ axis. Since, by definition, $\delta^{obsd}_{chel\text{-}H} = \delta_{OH}$ corresponds to the purely enolic and $\delta^{obsd}_{chel\text{-}H} = \delta_{SH}$ to the purely enethiolic state of existence, it follows that only that section of the double-branched hyperbolic curve lying between these two values has physical significance (Figure 2). A qualified fit of experimentally determined sets of variables $\delta^{obsd}_{chel\text{-}H}$, A_D/A_C to a hyperbola as defined by eq 4 would make up a nice verification of the physical reality of the (Z)-enol/(Z)-enethiol equilibrium system C ⇄ D, on condition, of course, that the hyperbolic parameters δ_{OH}, δ_{SH}, and ϵ_D/ϵ_C are physically meaningful.[59] However, having established the validity of eq 4, we

(53) Duus, F. *Tetrahedron* **1972**, *28*, 5923.
(54) Thimm, K.; Voss, J. *Z. Naturforsch.* **1974**, *29b*, 419.
(55) Bridges, A. J.; Whitham, G. H. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1603.
(56) Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry"; Harper and Row: New York, 1976; p 687.
(57) Martin, M. L.; Martin, G. J.; Delpuech, J.-J. "Practical NMR Spectroscopy"; Heyden: London, 1980; p 296.

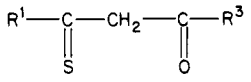
(58) (a) Sohár, P. "Nuclear Magnetic Resonance Spectroscopy"; CRC Press: Florida, 1983; Vol. 2, pp 99–113 and references cited therein. (b) Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. "High Resolution Nuclear Magnetic Resonance Spectroscopy"; Pergamon Press: Oxford, 1966; Vol. 2, pp 816 and 820 and references cited therein. (c) Emsley, J. "The Composition, Structure, and Hydrogen Bonding of the β-Diketones", in "Structure and Bonding"; Springer-Verlag: Germany, 1984; Vol. 57 p 147.

(59) Equations 1, 2, and 3 may be combined by yield alternatively eq 4a, which is easily derivable also from eq 4:

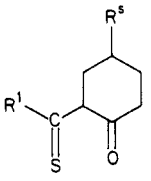
$$\frac{A_C}{A_D} = \frac{\epsilon_D}{\epsilon_C} \frac{\delta_{OH} - \delta^{obsd}_{chel\text{-}H}}{\delta^{obsd}_{chel\text{-}H} - \delta_{SH}} \quad (4a)$$

This equation describes the hyperbolic dependency of A_C/A_D on $\delta^{obsd}_{chel\text{-}H}$. In this case the assymptotes are defined by $\delta^{obsd}_{chel\text{-}H} = \delta_{SH}$ and $A_C/A_D = \epsilon_C/\epsilon_D$, $\delta^{obsd}_{chel\text{-}H} = \delta_{OH}$ marking the intersection of the hyperbola with the $\delta^{obsd}_{chel\text{-}H}$ axis. A choice between eq 4 and 4a may be indifferent or eventually (as in the present case) a question of how the experimentally determined data points, from a statistical point of view, most suitably define the two hyperbolas.

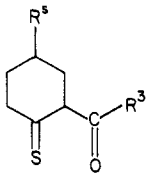
Chart I



1 Me/Me
2 Me/*i*-Bu
3 Me/CH_2-*t*-Bu
4 Me/cyclopropyl
5 Me/*i*-Pr
6 Me/*sec*-Bu
7 Me/cyclohexyl
8 Me/1-methylcyclopropyl
9 Me/*t*-Bu
10 Me/1-adamantyl
11 Et/Me
12 Et/Et
13 Et/*i*-Bu
14 Et/CH_2-*t*-Bu
15 Et/cyclopropyl
16 Et/*i*-Pr
17 Et/*sec*-Bu
18 Et/cyclohexyl
19 Et/1-methylcyclopropyl
20 Et/*t*-Bu
21 Et/1-adamantyl
22 Pr/Pr



23 Me/H
24 Me/Me
25 Me/*t*-Bu
26 Et/H
27 Et/Me
28 Et/*t*-Bu



29 H/Me
30 Me/Me
31 *t*-Bu/Me

may easily determine the actual equilibrium concentrations (i.e., the mole fractions) of the tautomeric constituents on the basis of either of the eq 5, 6, 7, and 8 (derivable from combining eq 1 and 2, or from eq 3):

$$x_C = \frac{\epsilon_D/\epsilon_C}{A_D/A_C + \epsilon_D/\epsilon_C} \quad (5)$$

$$x_D = \frac{A_D/A_C}{A_D/A_C + \epsilon_D/\epsilon_C} \quad (6)$$

$$x_C = \frac{\delta_{OH} - \delta^{obsd}_{chel\text{-}H}}{\delta_{OH} - \delta_{SH}} \quad (7)$$

$$x_D = \frac{\delta^{obsd}_{chel\text{-}H} - \delta_{SH}}{\delta_{OH} - \delta_{SH}} \quad (8)$$

Similarly, the equilibrium constants $K_{eq} = x_D/x_C$ for the C $\rightleftarrows$ D equilibria of the β-thioxo ketones concerned may be determined easily from eq 9 and 10 (derived by combining eqs 5 and 6, and 7 and 8, respectively):

$$K_{eq} = \frac{A_D/A_C}{\epsilon_D/\epsilon_C} \quad (9)$$

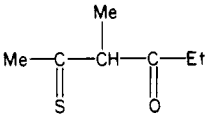
$$K_{eq} = \frac{\delta^{obsd}_{chel\text{-}H} - \delta_{SH}}{\delta_{OH} - \delta^{obsd}_{chel\text{-}H}} \quad (10)$$

Results and Discussion

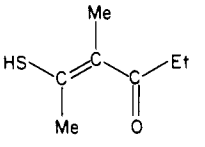
A satisfactory statistical basis for checking the validity of the above model was provided by the successful syntheses of 31 appropriate β-thioxo ketones (Chart I). All of these compounds display "single species" ^{1}H NMR spectra (i.e., weighted average spectra of those of the (*Z*)-enethiolic and (*Z*)-enolic constituents) and UV spectra characterized by well-defined $\pi \rightarrow \pi^*$ transition bands of the S—C=C—C=O and O—C=C—C=S systems, respectively. A few open-chain α-alkylated β-thioxo ketones were also synthesized[1] but not found appropriate for inclusion in this study, since their spectra clearly disclosed complex features (coexistence of the C $\rightleftarrows$ D system with the (*E*)-enethiol form A).[60] In order to approximate as closely as possible the ideality of the model, solute–solute interaction effects were virtually eliminated by recording the ^{1}H NMR spectra[61] as well as the UV spectra[62] of **1–31** on appropriately diluted solutions. Measurements were carried out with six different aprotic solvents: cyclohexane, tetrachloromethane, dioxane, dichloromethane, chloroform, and acetonitrile.[63] Pertinent ^{1}H NMR and UV data are listed in Table I.

Separate hyperbolic curve fit was carried out for each of the solvents by means of computational techniques. The parameters characterizing the respective hyperbolas (i.e., δ_{OH}, δ_{SH}, and ϵ_D/ϵ_C) are tabulated in Table II (approach A). In all cases the δ_{OH} values found appear to be very reliable and physically meaningful, a clear dependence on the solvent being notable. Also the ϵ_D/ϵ_C values seem reliable (the similarity of the two chromophore systems S—C=C—C=O and O—C=C—C=S predicts $\pi \rightarrow \pi^*$ transition probabilities of the same magnitude). However, the resulting δ_{SH} values are somewhat small as compared with for example δ_{SH} values found for hydrogen-bonded (*Z*)-enethiolic β-thioxo esters (δ_{SH} = 4–8).[17,53,64] In fact, they are even lower than δ_{SH} values found for non-hydrogen-bonded enethiols ((*E*)-enethiolic β-thioxo esters (δ_{SH} = 2.7–3.0)[53,64] or the (*E*)-enethiol form of 3-methyl-2-thioxohexan-4-one **32** (δ_{SH} = 2.65–3.48, Table II, column 6)). Nevertheless, the results imply immediately convincing qualitative evidence for the physical reality of the labile C $\rightleftarrows$ D equilibrium system.

The determination of δ_{SH} is obviously encumbered with the largest uncertainty (a small fortuitous change of the curvature, i.e., of ϵ_D/ϵ_C, may have a large effect on δ_{SH}). The relatively low δ_{SH} values found thus may be accidental if not simply a reflection of the deviation of the physical reality from the ideality of the model. On the other hand, it cannot be excluded that the low δ_{SH} values actually are physically meaningful. In that case we must conclude that the intramolecular hydrogen bonding in the (*Z*)-enethiol form C of β-thioxo ketones is a very weak one. This finding supports earlier suggestions.[28,44] However, for practicing determination of the site of the C $\rightleftarrows$ D equilibrium of any β-thioxo ketone, the δ_{SH} values found are inexpedient. The physical reality dictates the lower limit of δ_{SH} to be that of the proton of a freely rotating mercapto group. Fits, carried out on the basis of the data of the β-thioxo ketones **1–31**, subjected to the additional requirement of $\delta_{OH} > \delta_{SH} \geq \delta^{trans}_{SH}$, where δ^{trans}_{SH} refers to the mercapto-proton chemical shift of the nonchelating (*E*)-enethiol form (32A) of 3-methyl-2-thioxohexan-4-one (**32**)[60] determined at virtually infinite dilution in the respective solvents, lead to exactly $\delta_{SH} = \delta^{trans}_{SH}$ in all cases, moderately increased ϵ_D/ϵ_C values, but only slightly different δ_{OH} values (Table II, approach B). The acceptability of the latter, modified model (approach B) is demonstrated efficiently by the graphic representations shown in Figure 3.



32



32A

The constant attainment of remarkable low δ_{SH} values leads to the inevitable conclusion that the two-component system studied must be composed of on the one hand the strongly hydrogen-chelating (*Z*)-enol form (D) and on the other hand a (*Z*)-enethiol form, where intramolecular hydrogen bonding plays little or no

(60) The equilibrium systems of open-chain α-substituted β-thioxo ketones are the subject of a separate forthcoming paper.

(61) The chelate proton chemical shift of β-thioxo ketones may vary with the concentration of the solution. However, for solutions in the concentration range below slightly above 0.1 M it assumes a constant maximum value ($= \delta^{obsd}_{chel\text{-}H}$).

(62) The A_D/A_C ratio for every particular β-thioxo ketone in any of the six solvents at ambient temperature was checked repeatedly and found, without exceptions, to be virtually constant in the concentration range 2×10^{-4} to 5×10^{-6} M.

(63) The corresponding perdeuterated solvents were used in the ^{1}H NMR measurements.

(64) Duus, F. *Tetrahedron* **1974**, *30*, 3753.

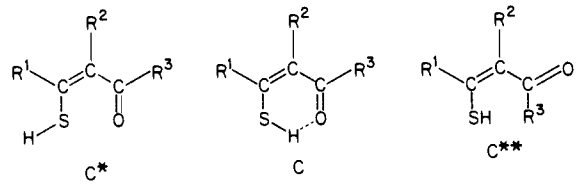
Table I. Calculated UV Absorbance Ratios A_D/A_C and Measured ^1H NMR Chelate-Proton Chemical Shifts of β-Thioxo Ketones 1–31[a]

		solvent[b]					
		C_6H_{12}	CCl_4	dioxane	CH_2Cl_2	$CHCl_3$	MeCN
1	A_D/A_C	3.03	2.68	1.73	1.39	1.25	1.28
	$\delta^{obsd}_{chel\text{-}H}$	13.96	13.53	12.45	11.53	11.48	10.95
2	A_D/A_C	3.87	3.38	2.26	2.02	1.86	1.61
	$\delta^{obsd}_{chel\text{-}H}$	14.30	13.88	12.85	12.23	12.19	11.36
3	A_D/A_C	5.09[c]	5.04[c]	3.16	2.87	2.60	1.98
	$\delta^{obsd}_{chel\text{-}H}$	14.81	14.61	13.68	13.22	13.18	12.44
4	A_D/A_C	1.76	1.77	1.14	1.11	1.01	1.08
	$\delta^{obsd}_{chel\text{-}H}$	13.09	12.85	11.71	10.93	10.78	10.32
5	A_D/A_C	2.82	2.50	1.59	1.36	1.24	0.94
	$\delta^{obsd}_{chel\text{-}H}$	13.92	13.50	12.16	11.38	11.31	10.41
6	A_D/A_C	3.16	3.07	1.94	1.73	1.56	1.25
	$\delta^{obsd}_{chel\text{-}H}$	14.24	13.81	12.63	11.96	11.85	11.03
7	A_D/A_C	3.50	3.15	2.11	1.72	1.60	1.27
	$\delta^{obsd}_{chel\text{-}H}$	14.29	13.95	12.78	12.09	11.98	11.18
8	A_D/A_C	4.45	4.20	2.36	2.17	1.94	1.62
	$\delta^{obsd}_{chel\text{-}H}$	14.48	14.18	12.75	11.91	11.77	10.99
9	A_D/A_C	3.13	2.98	1.57	1.43	1.33	0.95
	$\delta^{obsd}_{chel\text{-}H}$	14.07	13.62	11.90	11.06	10.96	9.91
10	A_D/A_C	5.20[c]	5.05[c]	2.58	2.26	2.18	1.48
	$\delta^{obsd}_{chel\text{-}H}$	14.88	14.47	13.02	12.33	12.19	11.20
11	A_D/A_C	3.43	3.06	2.36	1.79	1.40	1.66
	$\delta^{obsd}_{chel\text{-}H}$	14.41	14.18	13.18	12.23	12.13	11.83
12	A_D/A_C	3.10	2.83	2.00	1.55	1.38	1.41
	$\delta^{obsd}_{chel\text{-}H}$	14.05	13.78	12.57	11.73	11.60	11.12
13	A_D/A_C	4.60	4.11	3.10	2.58	2.29	2.11
	$\delta^{obsd}_{chel\text{-}H}$	14.71	14.34	13.50	12.88	12.79	12.26
14	A_D/A_C	5.83	6.05	4.59	3.97	3.70	3.23
	$\delta^{obsd}_{chel\text{-}H}$	15.14	14.84	14.22	13.79	13.69	13.24
15	A_D/A_C	2.14	2.14	1.70	1.37	1.24	1.25
	$\delta^{obsd}_{chel\text{-}H}$	13.64	13.34	12.39	11.60	11.49	11.10
16	A_D/A_C	3.49	3.22	2.13	1.79	1.58	1.46
	$\delta^{obsd}_{chel\text{-}H}$	14.40	14.00	12.91	12.12	12.00	11.37
17	A_D/A_C	4.01	3.84	2.43	2.28	2.02	1.74
	$\delta^{obsd}_{chel\text{-}H}$	14.66	14.30	13.33	12.66	12.50	11.87
18	A_D/A_C	4.19	3.88	2.79	2.31	2.11	1.80
	$\delta^{obsd}_{chel\text{-}H}$	14.73	14.40	13.48	12.75	12.62	12.08
19	A_D/A_C	4.95	4.65	3.25	2.65	2.40	1.99
	$\delta^{obsd}_{chel\text{-}H}$	14.90	14.61	13.52	12.71	12.54	12.07
20	A_D/A_C	3.74	3.48	2.07	1.78	1.64	1.26
	$\delta^{obsd}_{chel\text{-}H}$	14.64	14.22	12.73	11.96	11.84	10.92
21	A_D/A_C	5.27[c]	4.84	3.05	2.67	2.35	1.85
	$\delta^{obsd}_{chel\text{-}H}$	15.27	14.91	13.93	13.18	13.02	12.33
22	A_D/A_C	3.43	3.26	2.18	1.91	1.67	1.57
	$\delta^{obsd}_{chel\text{-}H}$	14.31	13.96	12.96	12.29	12.17	11.70
23	A_D/A_C	15.19[d]	10.71[d]	5.16[c]	3.82	3.21	3.65[c]
	$\delta^{obsd}_{chel\text{-}H}$	16.01	15.50	14.84	13.73	13.52	13.38
24	A_D/A_C	12.12[d]	9.93[c]	4.83[c]	3.86	2.98	2.69
	$\delta^{obsd}_{chel\text{-}H}$	15.98	15.60	14.91	13.80	13.54	13.49
25	A_D/A_C	14.82[d]	12.73[d]	6.39[c]	4.75	3.66	4.18
	$\delta^{obsd}_{chel\text{-}H}$	15.97	15.62	14.94	13.89	13.67	13.52
26	A_D/A_C	12.36[d]	10.51[d]	5.03[c]	3.39	2.83	2.96
	$\delta^{obsd}_{chel\text{-}H}$	16.17	15.80	14.90	13.69	13.51	13.27
27	A_D/A_C	9.83[d]	8.59[d]	4.30[c]	3.49	2.89	2.72
	$\delta^{obsd}_{chel\text{-}H}$	16.17	15.80	15.00	13.74	13.54	13.46
28	A_D/A_C	14.10[d]	10.61[d]	4.97[c]	3.93	3.04	3.01
	$\delta^{obsd}_{chel\text{-}H}$	16.18	15.80	15.10	13.87	13.65	13.68
29	A_D/A_C	0.41	0.37	0.17	0.13	0.13	0.15
	$\delta^{obsd}_{chel\text{-}H}$	7.19	6.63	5.12	4.38	4.43	4.28
30	A_D/A_C	0.39	0.33	0.21	0.14	0.15	0.15
	$\delta^{obsd}_{chel\text{-}H}$	7.09	6.62	5.14	4.41	4.42	4.32
31	A_D/A_C	0.43	0.37	0.22	0.18	0.18	0.17
	$\delta^{obsd}_{chel\text{-}H}$	7.13	6.43	5.12	4.37	4.39	4.28

[a] Unless specified otherwise, the UV absorbance ratios were reproducible within ±2%. The chelate-proton chemical shifts, corresponding to infinite dilution, were reproducible within ±0.02 ppm. Full UV and ^1H NMR spectral details are available as supplementary material. [b] The corresponding perdeuterated solvents were used by the ^1H NMR measurements. [c] Reproducibility within ±5%. [d] Reproducibility within ±10%.

part as a stabilizing factor.[65] Most probably, the realistic idea of the (*Z*)-enethiolic constituent implies a rotameric equilibrium system C* ⇄ C ⇄ C**, where the rotameric states C* and C** may be extensively populated, and where the rotameric interconversions proceed through energy barriers considerably lower than those connected with the (*Z*)-enol/(*Z*)-enethiol hydrogen-transfer process (see also the conclusion in ref 28). This idea does not necessarily violate the applicability of the two-component model, since the rotameric forms C, C*, and C** are expected to display practically nondiscernable UV spectra.[20] Thus the observed UV absorption band ascribed to a $\pi \rightarrow \pi^*$ transition

(65) That a mercapto group tends to avoid intramolecular hydrogen bonding to a suitably located carbonyl group is not unprecedented, as demonstrated recently by a ^1H NMR spectroscopic study of methyl *o*-mercaptobenzoate: Schaefer, T.; McKinnon, D. M.; Sebastian, R.; Krawchuk, B. *Can. J. Chem.*, **1981**, *59*, 566.



C* C C**

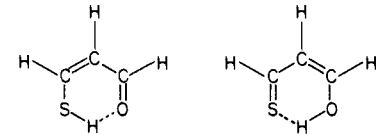
within the S—C=C—C=O chromophoric system of C alone[36] might be rather a superposition of related $\pi \rightarrow \pi^*$ bands from all rotameric enethiolic constituents. The simultaneous existence of rotameric enethiol forms has in fact already been suggested on the basis of dynamic ^{1}H NMR[28] and IR[19] evidences. Of course, the latter idea adds further uncertainty as to the definition of a "universal" δ_{SH} value, since the rotameric enethiol forms may be unequally populated for the individual β-thioxo ketone systems. Hence, the physical significance of the δ_{SH} value determined by the regression analysis (approach B) is less clear than that of the δ_{OH} value but within the scope of the underlying model δ_{SH} as determined according to approach B doubtless represents the best choice of a convenient standard reference.

On the basis of the hyperbolic parameters determined (approach B), we have calculated the equilibrium mole fractions x_D for all investigated simple β-thioxo ketones in any of the six solvents (Table III). Three features are immediately noticeable.

First, apart from the 2-acylcyclohexanethiones **29–31**, where the preference for formation of a molecular structure with an endocyclic rather than an exocyclic C=C double bond accounts for the predominance of the (*Z*)-enethiol form C,[20,66,67] the (*Z*)-enol form D is generally the predominant tautomeric constituent, i.e., other things being equal, the (*Z*)-enol form D doubtless represents the thermodynamically more stable state of existence. The preference of six-membered carbocyclics to form the endocyclic rather than the exocyclic double bond also manifests itself within the series of 2-thioacylcycloalkanones **23–28**, where particularly high x_D values are found.

Second, although the mechanism, by which the flanking groups R^1 and R^3 control the C $\rightleftarrows$ D equilibrium, is not immediately reflected by the tabulated x_D values, there is at least one striking regularity: Change of R^1 = Me to R^1 = Et within an otherwise unaltered β-thioxo ketone molecule effects a general enhancement of x_D, which is practically independent of the nature of R^3, although clearly dependent on the nature of the solvent. At present we cannot decide whether this effect is due to a relative stabilization of the (*Z*)-enol form (an increased negative charge on the sulfur atom of D resulting from increased electron release from R^1 effects strengthening of the intramolecular hydrogen bonding)[68,69] or to a relative destablization of the (*Z*)-enethiol form (change of R^1 = Me to R^1 = Et may lead to an increased sterically conditioned restriction of the rotation of the mercapto group, disfavoring the rotameric form C*). Perhaps both mechanisms are operative. It is anticipated that R^3 acts as equilibrium regulator by similar mechanisms. However, since the (*Z*)-enol tautomeric form evidently is represented solely by the intramolecularly hydrogen-bonded structure D (in contrst to the (*Z*)-enethiol form, where rotameric forms C* and C** may be of importance), it follows that the relative stability of merely the (*Z*)-enethiol form can be influenced by R^3. Thus R^3 can influence the strength of the (weak) intramolecular hydrogen bonding in C by inductive electron release and/or affect sterically the population of the rotameric form C**.[70]

Third, on changing the solvent from nonpolar cyclohexane and tetrachloromethane to solvents of higher polarity, a general decrease in the (*Z*)-enolic content can be observed. This clearly indicates that the other constituent, the (*Z*)-enethiol form, is the more polar of the two tautomeric forms, which is exactly what has been predicted by CNDO/S-CI calculations carried out on the hydrogen-bonding (*Z*)-enethiol and (*Z*)-enol forms (33C and 33D, respectively) of monothiomalondialdehyde:[71]



33C $\vec{\mu}_{calcd}$ = 4.52 D **33D** $\vec{\mu}_{calcd}$ = 4.20 D

Table II. Computable Parameters δ_{OH}, δ_{SH}, and ϵ_D/ϵ_C[a]

solvent	approach A[b]			approach B[c]		
	δ_{OH}	δ_{SH}	ϵ_D/ϵ_C	δ_{OH}	δ_{SH}	ϵ_D/ϵ_C
C_6H_{12}	16.75	0.15	0.58	16.78	2.65	0.73
CCl_4	16.50	0.43	0.60	16.55	2.74	0.74
dioxane	16.65	1.71	0.72	16.78	3.48	0.89
CH_2Cl_2	15.65	1.41	0.60	15.76	2.93	0.73
$CHCl_3$	15.58	0.84	0.52	15.75	2.87	0.67
MeCN	15.49	0.41	0.53	15.73	3.32	0.77

[a] Determined by hyperbolic curve fit of data sets ($\delta^{obsd}_{chel\cdot H}$, A_D/A_C) according to eq 4. [b] No additional requirements. [c] Additional requirement: $\delta_{OH} > \delta_{SH} \geq \delta^{trans}_{SH}$, where δ^{trans}_{SH} refers to the mercapto-proton chemical shift of the non-proton-chelating (*E*)-enethiol form (A) (trans-form) of 3-methyl-2-thioxohexan-4-one in the respective solvents at infinite dilution. In all cases the computations gave $\delta_{SH} = \delta^{trans}_{SH}$

Table III. Calculated Mole Fractions x_D of the (*Z*)-Enol Form (D) Coexisting in Tautomeric Equilibrium with the (*Z*)-Enethiol Form (C) in Virtually Infinitely Diluted Solutions of Simple β-Thioxo Ketones **1–31** at Ambient Temperature[a]

compd	solvent					
	C_6H_{12}	CCl_4	dioxane	CH_2Cl_2	$CHCl_3$	MeCN
1D	0.80	0.78	0.67	0.66	0.66	0.62
2D	0.83	0.81	0.71	0.73	0.73	0.66[b]
3D	0.87	0.87	0.77	0.80	0.80	0.73
4D	0.72[b]	0.72[b]	0.59[c]	0.61	0.61	0.57
5D	0.80	0.78	0.65	0.66	0.65	0.56
6D	0.82	0.80	0.69	0.70	0.70	0.62
7D	0.83	0.81	0.70	0.71	0.71	0.63
8D	0.85	0.84	0.71[b]	0.72[c]	0.72[c]	0.65[c]
9D	0.81	0.80	0.64	0.65[b]	0.65[b]	0.54
10B	0.87	0.86	0.73	0.74	0.74[b]	0.65
11D	0.83	0.82	0.73	0.72	0.70[b]	0.68
12D	0.80	0.80	0.69	0.68	0.68	0.64
13D	0.86	0.84	0.77[b]	0.79	0.77	0.73
14D	0.89	0.88	0.82[b]	0.85	0.84	0.80
15D	0.76[b]	0.76[b]	0.66	0.66[b]	0.66	0.62
16D	0.83	0.81	0.71	0.71	0.71	0.65
17D	0.85	0.84	0.74	0.76	0.75	0.70
18D	0.85	0.84	0.76	0.76	0.76	0.70
19D	0.87	0.86	0.77[b]	0.77	0.77[b]	0.71
20D	0.84	0.83	0.70	0.71	0.70	0.62
21D	0.89	0.87	0.78	0.79	0.78	0.72
22D	0.83	0.81	0.71	0.73	0.72	0.67
23D	0.95	0.93	0.85	0.84	0.83	0.82
24D	0.94	0.93	0.85	0.84	0.82	0.80[b]
25D	0.95	0.94	0.87	0.86	0.84	0.83
26D	0.95	0.94	0.85	0.83	0.82	0.80
27D	0.94[b]	0.93[b]	0.85[b]	0.84	0.82	0.80[b]
28D	0.95	0.94	0.86	0.85	0.83	0.82[b]
29D	0.34[b]	0.31[c]	0.14[b]	0.13[b]	0.14[b]	0.12[d]
30D	0.33[b]	0.30[b]	0.16[c]	0.14[b]	0.15[c]	0.12[d]
31D	0.34[c]	0.30[c]	0.16[d]	0.16[d]	0.17[d]	0.13[d]

[a] The listed x_D's are the average values of those determined from eq 6 and 8, respectively, using the hyperbolic parameters determined according to approach B. Unless specified otherwise, deviations are not exceeding ±0.01. [b] Deviation not exceeding ±0.02. [c] Deviation not exceeding ±0.03. [d] Deviation not exceeding ±0.05.

(66) Brown, H. C.; Brewster, J. H.; Shechter, H. *J. Am. Chem. Soc.* **1954**, *76*, 467.
(67) Gorodetsky, M.; Luz, Z.; Mazur, Y. *J. Am. Chem. Soc.* **1967**, *89*, 1183.
(68) Kollman, P. A.; Allen, L. C. *Chem. Rev.* **1972**, *72*, 283.
(69) Schuster, P. *Z. Chem.* **1973**, *13*, 41.
(70) A closer examination of the regulating capabilities of R^1 and R^3 is in progress.
(71) Carlsen, L.; Duus, F., unpublished details from previously reported CNDO/S-CI calculations (see ref 37).

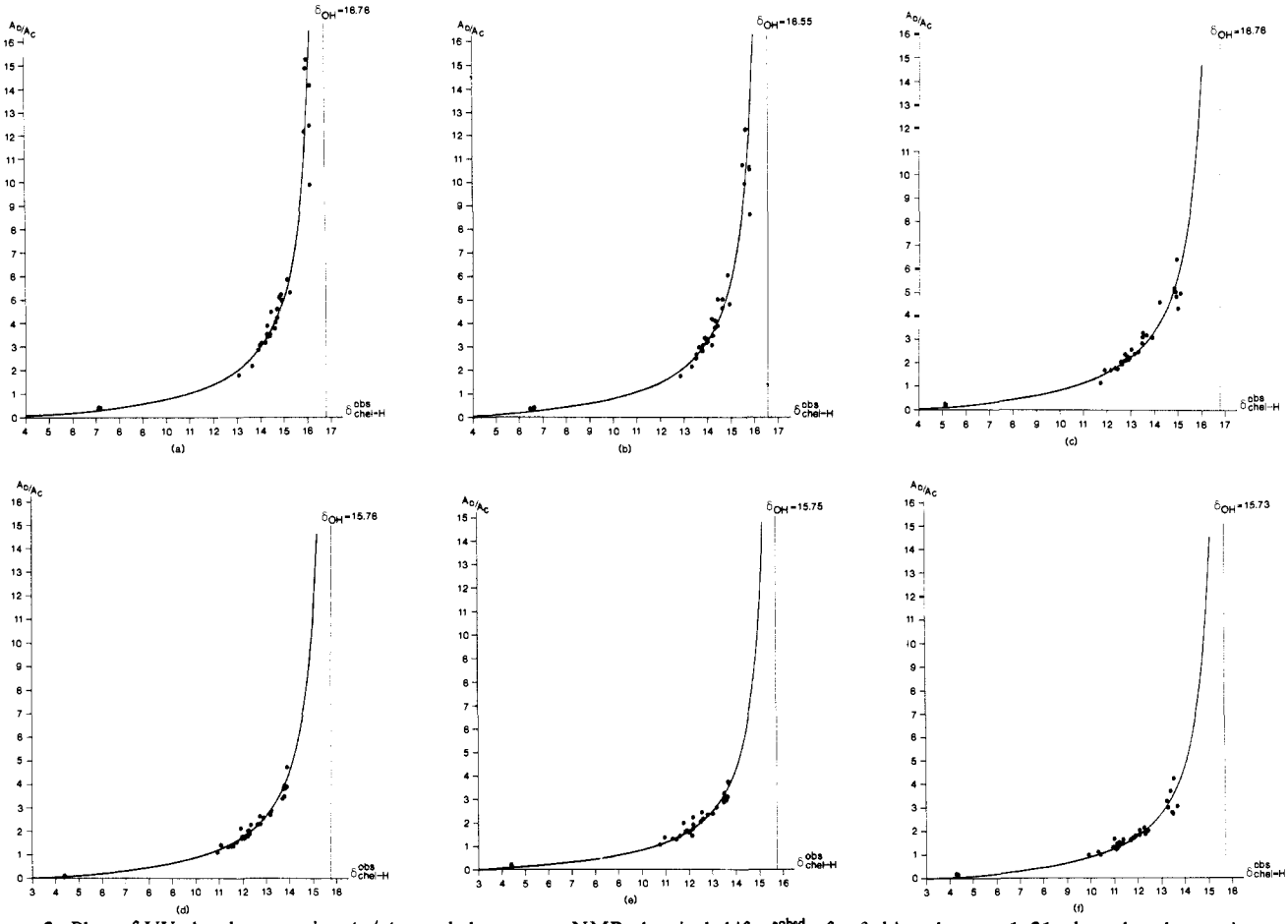


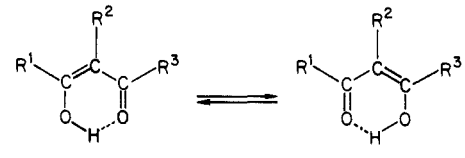
Figure 3. Plots of UV absorbance ratios A_D/A_C vs. chelate proton NMR chemical shifts δ^{obsd}_{chel-H} for β-thioxo ketones **1–31** adapted to the requirement of hyperbolic coherence according to eq 4 and the restriction $\delta_{OH} > \delta_{SH} \geq \delta^{trans}_{SH}$ (approach B). Solvents: (a) cyclohexane, (b) tetrachloromethane, (c) dioxane, (d) dichloromethane, (e) chloroform, (f) acetonitrile.[63]

On the basis of eq 9 and 10 equilibrium constants for the C ⇄ D system of all 31 β-thioxo ketones in any of the six solvents have been calculated. These values have been used to evaluate the energetics connected with the (*Z*)-enethiol/(*Z*)-enol interconversion process in terms of the standard free energy

$$\Delta G^\circ = -RT \ln K_{eq} \qquad (11)$$

The tabulated standard free energies (Table IV) have been calculated by using T = 301 K, the "average ambient temperature". For practical reasons, the ^{1}H NMR and UV spectra were recorded at different "ambient" temperatures (see Experimental Section). However, the additional uncertainty introduced by using the "average ambient temperature" is modest, as seen from the tabulated maximum uncertainties (Table IV).[72]

Much work, theoretical[69,73] as well as experimental,[67,74-76] has been performed to substantiate the occurrence of the related (*Z*)-enol/(*Z*)-enol tautomerism of β-oxoaldehydes and β-oxo



ketones.[77] Since the central chelate systems of the two interconverting forms are formally identical, the site of the (*Z*)-enol/(*Z*)-enol equilibrium depends alone on the relative stabilities of the respective molecular frameworks, i.e., on the nature of R^1, R^2, and R^3. For $R^1 = R^3$ the equilibrium system is to be represented by a symmetrical double well potential function,[78] and the interconversion process is characterized thermodynamically by $\Delta G^\circ = 0$. For $R^1 \neq R^3$, we have $\Delta G^\circ \neq 0$. Furthermore, unsymmetrical substitution (i.e., $R^1 \neq R^3$) may effect a difference

(72) The weighted average chelate proton shift δ^{obsd}_{chel-H} changes with the temperature, a lowering of the temperature effecting increase of δ^{obsd}_{chel-H} for compounds **1–28**, decrease of δ^{obsd}_{chel-H} for compounds **29–31**, and vice versa (see ref 28). Around 300 K, within a temperature interval of ca. 20 centigrade degrees, δ^{obsd}_{chel-H} depends approximately linearly on the temperature. The change in δ^{obsd}_{chel-H} per degree ($\Delta\delta$) is somewhat influenced by the nature of the β-thioxo ketone and the solvent. Consultative experiments gave $\Delta\delta = -0.010 \pm 0.003$ ppm/deg for the compounds **1–28**, $\Delta\delta = 0.006 \pm 0.002$ ppm/deg for the compounds **29–31**. Thus, in general, the error introduced by adapting to 301 K the chelate proton shift values determined at 308 K amounts to less than 0.1 ppm, which is acceptable in view of the approximations made otherwise (e.g., disregard of intramolecular shielding from R^1, R^2, and R^3).

(73) (a) Karlström, G.; Wennerström, H.; Jonsson, B.; Forsén, S.; Almlöf, J.; Roos, B. *J. Am. Chem. Soc.* **1975**, *97*, 4188. (b) Fluder, E. M.; de la Vega, J. R. *Ibid.* **1978**, *100*, 5265. (c) Catalan, J.; Yáñez, M.; Fernandez-Alonso, J. I. *Ibid.* **1978**, *100*, 6917. (d) de la Vega, J. R.; Busch, J. H.; Schauble, J. H.; Kunze, K. L.; Haggert, B. E. *Ibid.* **1982**, *104*, 3295. (e) de la Vega, J. R. *Acc. Chem. Res.* **1982**, *15*, 185. (f) Bicerano, J.; Schaefer, H. F.; Miller, W. H. *J. Am. Chem. Soc.* **1983**, *105*, 2550.

(74) Forsén, S.; Nilsson, M. In "The Chemistry of the Carbonyl Group"; Zabicky, J., Ed.; Interscience: New York, 1970; Vol. 2, Chapter 3, p 207 and references therein.

(75) (a) Terpinski, J.; Kozluk, T. *Rocz. Chem.* **1974**, *48*, 29. (b) Shapet'ko, N. N.; Radushnova, I. L.; Bogachev, Y. S.; Berestova, S. S.; Potapov, V. M.; Kiryuschkina, G. V.; Talebarovskaya, I. K. *Org. Magn. Reson.* **1975**, *7*, 540. (c) Rowe, W. F.; Duerst, R. W.; Wilson, E. B. *J. Am. Chem. Soc.* **1976**, *98*, 4021. (d) Egan, W.; Gunnarsson, G.; Bull, T. E.; Forsén, S. *Ibid.* **1977**, *99*, 4568. (e) Barna, J. C. J.; Robinson, M. J. T. *Tetrahedron Lett.* **1979**, 1455. (f) Kirsch, G.; Mieloszynski, J. L.; Paquer, D.; Andrieu, C. G. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 489.

(76) Noy, R. S.; Gindin, V. A.; Ershov, B. A.; Kol'tsov, A. I.; Zubkov, V. A. *Org. Magn. Reson.* **1975**, *7*, 109.

(77) For deviant views, see: (a) Bratan, S.; Strohbusch, F. *Chem. Ber.* **1972**, *105*, 2284. (b) Shapet'ko, N. N. *Org. Magn. Reson.* **1973**, *5*, 215. (c) Shapet'ko, N. N.; Berestova, S. S.; Lukovkin, G. M.; Bogachev, Y. S. *Org. Magn. Reson.* **1975**, *7*, 237.

(78) Strictly speaking, this is necessarily true only when R^2, by nature, is not able to influence the symmetry of the whole molecule, as will be the case, for example, for R^2 = Me. For an excellent discussion of the latter situation, see ref 70e.

Table IV. Calcualted Standard Free Energies $\Delta G^\circ = -RT \ln E_{eq}$ (kcal/mol) for the (*Z*)-Enethiol/(*Z*)-Enol Tautomeric Equilibrium System C ⇄ D of β-Thioxo Ketones **1–31** in Different Solvents at Ambient Temperature (301 K)[a]

	solvent					
compd	C_6H_{12}	CCl_4	dioxane	CH_2Cl_2	$CHCl_3$	MeCN
1	−0.84 ± 0.03	−0.77 ± 0.02	−0.42 ± 0.03	−0.41 ± 0.03	−0.40 ± 0.03	−0.29 ± 0.02
2	−0.96 ± 0.06	−0.88 ± 0.05	−0.54 ± 0.03	−0.59 ± 0.03	−0.59 ± 0.04	−0.41 ± 0.05
3	−1.13 ± 0.06	−1.12 ± 0.06	−0.74 ± 0.04	−0.83 ± 0.03	−0.82 ± 0.03	−0.59 ± 0.04
4	−0.58 ± 0.06	−0.56 ± 0.06	−0.22 ± 0.07	−0.28 ± 0.03	−0.26 ± 0.02	−0.18 ± 0.03
5	−0.81 ± 0.03	−0.73 ± 0.04	−0.36 ± 0.03	−0.38 ± 0.02	−0.38 ± 0.02	−0.15 ± 0.03
6	−0.89 ± 0.04	−0.84 ± 0.03	−0.47 ± 0.02	−0.52 ± 0.02	−0.50 ± 0.02	−0.28 ± 0.02
7	−0.93 ± 0.03	−0.87 ± 0.02	−0.51 ± 0.02	−0.53 ± 0.03	−0.53 ± 0.02	−0.31 ± 0.03
8	−1.03 ± 0.08	−0.99 ± 0.07	−0.54 ± 0.06	−0.58 ± 0.08	−0.56 ± 0.09	−0.37 ± 0.09
9	−0.87 ± 0.03	−0.81 ± 0.04	−0.33 ± 0.02	−0.37 ± 0.05	−0.36 ± 0.06	−0.10 ± 0.03
10	−1.14 ± 0.06	−1.09 ± 0.08	−0.60 ± 0.06	−0.64 ± 0.05	−0.64 ± 0.08	−0.36 ± 0.04
11	−0.94 ± 0.04	−0.90 ± 0.07	−0.59 ± 0.02	−0.56 ± 0.04	−0.51 ± 0.08	−0.46 ± 0.02
12	−0.86 ± 0.03	−0.82 ± 0.03	−0.47 ± 0.03	−0.46 ± 0.02	−0.44 ± 0.02	−0.34 ± 0.03
13	−1.08 ± 0.05	−1.01 ± 0.04	−0.71 ± 0.06	−0.75 ± 0.03	−0.73 ± 0.02	−0.59 ± 0.03
14	−1.23 ± 0.04	−1.22 ± 0.07	−0.92 ± 0.08	−1.02 ± 0.03	−1.01 ± 0.04	−0.84 ± 0.04
15	−0.70 ± 0.07	−0.68 ± 0.06	−0.41 ± 0.03	−0.41 ± 0.04	−0.40 ± 0.04	−0.30 ± 0.02
16	−0.95 ± 0.03	−0.88 ± 0.03	−0.53 ± 0.02	−0.55 ± 0.02	−0.52 ± 0.02	−0.38 ± 0.02
17	−1.03 ± 0.03	−0.98 ± 0.02	−0.64 ± 0.06	−0.68 ± 0.02	−0.66 ± 0.02	−0.48 ± 0.02
18	−1.05 ± 0.04	−1.00 ± 0.03	−0.67 ± 0.03	−0.70 ± 0.03	−0.69 ± 0.02	−0.52 ± 0.02
19	−1.13 ± 0.04	−1.09 ± 0.03	−0.73 ± 0.07	−0.74 ± 0.05	−0.71 ± 0.07	−0.55 ± 0.04
20	−1.00 ± 0.05	−0.94 ± 0.04	−0.50 ± 0.02	−0.53 ± 0.02	−0.52 ± 0.03	−0.28 ± 0.02
21	−1.23 ± 0.07	−1.16 ± 0.06	−0.76 ± 0.04	−0.80 ± 0.04	−0.77 ± 0.03	−0.56 ± 0.05
22	−0.93 ± 0.02	−0.88 ± 0.03	−0.54 ± 0.02	−0.59 ± 0.03	−0.56 ± 0.03	−0.43 ± 0.02
23	−1.76 ± 0.10	−1.55 ± 0.09	−1.06 ± 0.03	−1.00 ± 0.03	−0.94 ± 0.02	−0.90 ± 0.05
24	−1.68 ± 0.04	−1.56 ± 0.04	−1.05 ± 0.06	−1.01 ± 0.04	−0.92 ± 0.04	−0.83 ± 0.10
25	−1.74 ± 0.10	−1.64 ± 0.10	−1.14 ± 0.07	−1.09 ± 0.06	−1.00 ± 0.04	−0.97 ± 0.07
26	−1.78 ± 0.12	−1.65 ± 0.10	−1.06 ± 0.04	−0.95 ± 0.06	−0.90 ± 0.06	−0.82 ± 0.03
27	−1.72 ± 0.20	−1.60 ± 0.16	−1.04 ± 0.11	−0.97 ± 0.05	−0.91 ± 0.05	−0.83 ± 0.09
28	−1.82 ± 0.09	−1.65 ± 0.10	−1.10 ± 0.09	−1.03 ± 0.05	−0.94 ± 0.06	−0.90 ± 0.10
29	0.39 ± 0.10	0.48 ± 0.09	1.06 ± 0.13	1.13 ± 0.13	1.06 ± 0.15	1.18 ± 0.33
30	0.41 ± 0.07	0.52 ± 0.06	0.99 ± 0.20	1.10 ± 0.15	1.03 ± 0.19	1.18 ± 0.31
31	0.38 ± 0.09	0.50 ± 0.12	0.99 ± 0.21	0.99 ± 0.27	0.96 ± 0.27	1.13 ± 0.39

[a] The deviations listed are maximum values calculated on the basis of the uncertainties connected with K_{eq} as well as *T*.

in efficiency between the intramolecular hydrogen bondings of the two forms. However, accepting ΔS°, the standard entropy change connected with the (*Z*)-enol/(*Z*)-enol interconversion process, as a reflector of mainly this difference, it can be concluded that substituents influence the strength of the hydrogen bonding only modestly, since the reported ΔS° values are numerically small (up to 2.0 cal/(mol·deg)).[76]

For the (*Z*)-enol/(*Z*)-enethiol tautomeric couple the situation is different. The (*Z*)-enol central system with its strong intramolecular hydrogen bonding is to be endowed with a relatively rigid, planar structure, whereas the (*Z*)-enethiol central system, owing to its considerably weaker hydrogen bonding, doubtless possesses a more fidgety planarity, existing perhaps even as rotamers C* and C**. Hence, we can predict the standard entropy change connected with the process C → D to be negative and numerically essentially larger than that for the (*Z*)-enol/(*Z*)-enol conversion. The fact that ΔS° values ranging from −6.8 to −25.1 cal/(mol·deg) have been determined for the (*Z*)-enethiol → (*Z*)-enol process of aromatic β-thioxo ketones (R^1, R^3 = aryl, R^2 = H) supports this anticipation.[37] On the basis of the relation

$$\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ$$

we predict the standard enthalpies, ΔH°, for the C → D processes to be lowered by some kcal/mol relative to the ΔG° values calculated (Table IV), depending, of course, eventually on contributions from simultaneous changes within the molecular framework.

Epilogue

With this work we have introduced a potential tool for the quantitative description of equilibria between two tautomeric forms displaying on the one hand individual UV spectra and on the other hand, in consequence of the rapidity of their interconversion, a weighted average ^{1}H NMR spectrum. The adaptation of appropriate UV and ^{1}H NMR observables into a simplified model of the tautomeric system, in this case the β-thioxo ketone (*Z*)-enol/(*Z*)-enethiol system, thus lead to determination of equilibrium constants and standard free energies of interconversion. An extension of the procedure to comprise also the response of temperature would lead to determination of standard enthalpies and entropies.[79] As implicitly suggested already, we anticipate fundamental applicability of the described procedure. Thus, the perspective comprise not only the applicability to other appropriate two-component systems but also a versatility with respect to the underlying spectroscopic techniques, a most obvious variation being replacement of the ^{1}H NMR observable by a ^{13}C NMR analogue.

Experimental Section

^{1}H NMR spectra were recorded on 0.1 M solutions of the β-thioxo ketones on a Jeol FX 90Q spectrometer (solutions in C_6D_{12}, dioxane-d_8, CD_2Cl_2, $CDCl_3$, and CD_3CN) at 308 K or on a Varian HA 100 spectrometer (solutions in CCl_4) at 303 K.

UV spectra were measured on a Beckman Acta III spectrophotometer at 295 K.

Three methods were used for the preparation of the β-thioxo ketones, of which only a few had been reported prior to this work. Physical characteristics for all unreported compounds are given below. The yields refer to the analytically pure, distilled or recrystallized products.

Method A: The corresponding β-diketone dissolved in acetonitrile was treated with gaseous hydrogen sulfide and hydrogen chloride at −35 to −40 °C as described previously for the preparation of **thioacetylacetone (1)**[19] and **2-acetylcyclohexanethione (29)**.[20] This method applies to open-chain α-unsubstituted β-thioxo ketones having identical flanking groups ($R^1 = R^3$) and to 2-acetylcyclohexanethiones.

5-Thioxoheptan-3-one (12): yellow oil; bp 91–92 °C (15 mmHg); yield 47%. Anal. Calcd for $C_7H_{12}OS$: C, 58.31; H, 8.39; S, 22.20. Found: C, 57.67; H, 8.59; S, 22.23.

6-Thioxononan-4-one (22): yellow oil; bp 73 °C (0.2 mmHg); yield 80%. Anal. Calcd for $C_9H_{16}OS$: C, 62.76; H, 9.36; S, 18.58. Found: C, 62.92; H, 9.53; S, 18.30.

2-Acetyl-4-methylcyclohexanethione (30): yellow oil; bp 83–84 °C (0.1 mmHg); yield 55%. Anal. Calcd for $C_9H_{14}OS$: C, 63.51; H, 8.29; S, 18.80. Found: C, 63.46; H, 8.16; S, 18.70.

2-Acetyl-4-*tert*-butylcyclohexanethione (31): yellow oil; bp 99–100 °C (0.16 mmHg); yield 32%. Anal. Calcd for $C_{12}H_{20}OS$: C, 67.89; H,

(79) Atkins, P. W. "Physical Chemistry"; Oxford University Press: Oxford, 1978; p 260.

9.50; S, 15.07. Found: C, 67.85; H, 9.74; S, 14.81.

Method B: Claisen condensation reaction of methyl ketones with thionoesters using sodium amide as base as described previously for the preparation of aromatic β-thioxo ketones (R^1 and/or R^3 = aryl, R^2 = H),[9] **2-thioacetylcyclohexanone (23)**,[20] and **1-(1-methylcyclopropyl)-3-thioxobutan-1-one (8)**.[44] The method applies apparently generally to 2-thioacylcycloalkanones and, with limitations, to open-chain β-thioxo ketones.[1]

2-Methyl-6-thioxoheptan-4-one (2): yellow oil; bp 42 °C (0.15 mmHg); yield 77%. Anal. Calcd for $C_8H_{14}OS$: C, 60.74; H, 8.92; S, 20.23. Found: C, 60.64; H, 9.05; S, 19.62.

1-Cyclopropyl-3-thioxobutan-1-one (4): yellow oil; bp 103-104 °C (13 mmHg); yield 63%. Anal. Calcd for $C_7H_{10}OS$: C, 59.12; H, 7.09; S, 22.95. Found: C, 59.06; H, 6.95; S, 22.52.

2-Methyl-5-thioxohexan-3-one (5): yellow oil; bp 75-76 °C (10 mmHg); yield 41%. Anal. Calcd for $C_7H_{12}OS$: C, 58.31; H, 8.39; S, 22.20. Found: C, 58.55; H, 8.51; S, 22.02.

4-Thioxohexan-2-one (11): yellow oil; bp 67-68 °C (9 mmHg); yield 52%. Anal. Calcd for $C_6H_{10}OS$: C, 55.37; H, 7.75; S, 24.59. Found: C, 55.31; H, 7.85; S, 24.60.

2-Methyl-6-thioxooctan-4-one (13): yellow oil; bp 65-66 °C (0.2 mmHg); yield 67%. Anal. Calcd for $C_9H_{16}OS$: C, 62.76; H, 9.36; S, 18.58. Found: C, 63.22; H, 9.62; S, 18.55.

1-Cyclopropyl-3-thioxopentan-1-one (15): yellow oil; bp 58 °C (0.14 mmHg); yield 34%. Anal. Calcd for $C_8H_{12}OS$: C, 61.52; H, 7.75; S, 20.49. Found: C, 61.61; H, 7.80; S, 19.95.

2-Methyl-5-thioxoheptan-3-one (16): yellow oil; bp 53-55 °C (0.25 mmHg); yield 37%. Anal. Calcd for $C_8H_{14}OS$: C, 60.74; H, 8.92; S, 20.23. Found: C, 60.74; H, 9.03; S, 19.65.

2-Thioacetyl-4-methylcyclohexanone (24): yellow oil; bp 98-99 °C (0.35 mmHg); yield 45%. Anal. Calcd for $C_9H_{14}OS$: C, 63.51; H, 8.29; S, 18.80. Found: C, 63.42; H, 8.52; S, 18.81.

2-Thioacetyl-4-*tert*-butylcyclohexanone (25): light yellow crystals; mp 58-59 °C (hexane); yield 44%. Anal. Calcd for $C_{12}H_{20}OS$: C, 67.89; H, 9.50; S, 15.07. Found: C, 68.08; H, 9.55; S, 14.90.

2-Thiopropionylcyclohexanone (26): yellow oil; bp 85 °C (0.2 mmHg); yield 63%. Anal. Calcd for $C_9H_{14}OS$: C, 63.51; H, 8.29; S, 18.80. Found: C, 63.61; H, 8.31; S, 18.22.

2-Thiopropionyl-4-methylcyclohexanone (27): yellow oil; bp 97 °C (0.3 mmHg); yield 48%. Anal. Calcd for $C_{10}H_{16}OS$: C, 65.19; H, 8.75; S, 17.36. Found: C, 65.42; H, 8.78; S, 17.17.

2-Thiopropionyl-4-*tert*-butylcyclohexanone (28): yellow oil; bp 138 °C (0.4 mmHg); yield 47%. Anal. Calcd for $C_{13}H_{22}OS$: C, 68.99; H, 9.80; S, 14.14. Found: C, 68.86; H, 9.98; S, 14.00.

Method C: Claisen condensation reaction of methyl ketones with thionoesters with *t*-BuLi as base, as described in the preliminary paper.[1] This method was developed as a direct consequence of the synthetic requirements set up by the intentions of this work. As demonstrated[1] by the successful syntheses of **2,2-dimethyl-6-thioxoheptan-4-one (3)**, **5-methyl-2-thioxoheptan-4-one (6)**, **1-cyclohexyl-3-thioxobutan-1-one (7)**, **2,2-dimethyl-5-thioxohexan-3-one (9)**, **1-(1-adamantyl)-3-thioxobutan-1-one (10)**, **2,2-dimethyl-6-thioxooctan-4-one (14)**, **3-methyl-6-thioxooctan-4-one (17)**, **1-cyclohexyl-3-thioxopentan-1-one (18)**, **1-(1-methylcyclopropyl)-3-thioxopentan-1-one (19)**, **2,2-dimethyl-5-thioxoheptan-3-one (20)**, and **1-(1-adamantyl)-3-thioxopentan-1-one (21)**, this method is superior to method B not only with respect to broadness of applicability but also as regards yields. **3-Methyl-2-thioxohexan-4-one (32)** was obtained in good yield by method B as well as by method C.[1]

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Registry No. 1, 14660-20-9; **2**, 99618-89-0; **3**, 99618-90-3; **4**, 99618-91-4; **5**, 99618-92-5; **6**, 99618-93-6; **7**, 99618-94-7; **8**, 87505-88-2; **9**, 15591-64-7; **10**, 99618-95-8; **11**, 81674-19-3; **12**, 57711-65-6; **13**, 99618-96-9; **14**, 99618-97-0; **15**, 99618-98-1; **16**, 99618-99-2; **17**, 99619-00-8; **18**, 99619-01-9; **19**, 99619-02-0; **20**, 99619-03-1; **21**, 99619-04-2; **22**, 99619-05-3; **23**, 15578-82-2; **24**, 99619-06-4; **25**, 99619-07-5; **26**, 99619-08-6; **27**, 99619-09-7; **28**, 99619-10-0; **29**, 76698-82-3; **30**, 99619-11-1; **31**, 99619-12-2.

Supplementary Material Available: Tables of complete UV and ^1H NMR spectra data for β-thioxo ketones **1-31** (25 pages). Ordering information is given on any current masthead page.

Dissociative Electron Transfer. Homogeneous and Heterogeneous Reductive Cleavage of the Carbon-Halogen Bond in Simple Aliphatic Halides

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Abstract: The kinetics of the reductive cleavage of the carbon-halogen bond in a series of *n*-, *sec*-, and *tert*-butyl halides are investigated as an example of dissociative electron-transfer processes. The heterogeneous (direct electrochemical reduction at an inert electrode) and homogeneous (electrochemical reduction mediated by aromatic anion radicals) cleavages were found to obey the same activation-driving force free-energy relationship. It is consistent with a concerted electron transfer-bond breaking mechanism, having as the origin of the driving force scale the standard potential of the $RX/R\cdot + X^-$. The activation-driving force relationship is nonlinear and can be approximated by a Hush-Marcus-type quadratic equation. When varying the halogen, from Cl to Br and to I, the reductive cleavage is both thermodynamically easier and kinetically faster at the standard state. The kinetics thus amplifies the thermodynamics in governing reduction potential $RX/R\cdot + X^-$ a given current density. While the essential factor determining the standard potential of the $RX/R\cdot + X^-$ couple is the energy of the carbon halogen bond, the standard activation free energy appears as mainly governed by the ease of the carbon-halogen bond stretching.

The reductive cleavage of the carbon-halogen bond in aliphatic halides (RX) upon addition of one electron is one of the simplest examples of dissociative electron transfer in the organic field. Unlike the case of aromatic halides,[2] there is evidence that a

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