Experimental Section

Melting points were determined on a Thomas-Hoover "Uni-Melting" apparatus and are uncorrected. Infrared spectra were determined on a Perkin-Elmer 21 spectrometer in Nujol. Nmr spectra were obtained on a Varian A-60 spectrometer in $CDCl_3$, with $(CH_3)_4Si$ as the internal standard. Mass spectra were determined on an AEI-MS-902 mass spectrometer.

Δ^2,α-Adamantaneacetic Acid (3).—To a well-stirred suspension of 21.8 g (0.45 mol) of sodium hydride (NaH) in 300 ml of dry 1,2-dimethoxyethane (DME), 100.9 g (0.45 mol) of triethyl phosphonoacetate was added slowly at 20°. After stirring for 2 hr at room temperature, a solution of 45.0 g (0.3 mol) of **1** in 450 ml of dry DME was added rapidly. The reaction mixture was maintained at 45° for 2 hr and then stirred overnight at room temperature. The mixture was concentrated, diluted with water, and extracted with ether. The ether extract was washed with water, dried ($MgSO_4$), and concentrated to give 65.5 g (99%) of **2** as a thick yellow liquid, ir 5.83 (C=O), 6.08 μ (conjugated C=C).

The crude ester **2** was hydrolyzed by refluxing with 300 ml of 5 *N* alcoholic KOH for 4 hr. The basic solution was cooled, acidified with 5 *N* HCl, and extracted with $CHCl_3$. The $CHCl_3$ solution was dried ($MgSO_4$) and evaporated *in vacuo* to give 56.6 g (98%) of **3** as brownish-white powder. Crystallization from dilute acetone gave an analytical sample: mp 136–138°; ir 3.70–4.00 (bonded OH), 5.90 (C=O), 6.10 μ (conjugated C=C); nmr τ 4.38 (s, 1, vinyl H), 5.83–6.05 (br, 1, OH), 7.37–7.66 (br, 2, CH adjacent to C=C), 7.83–8.25 (s, 12 H).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.19; H, 8.49.

2-Adamantaneacetic Acid (4).—A solution of 9.6 g (0.05 mol) of **3** in C_2H_5OH containing 1 equiv of 5 *N* NaOH was hydrogenated over 5% Pd/C. After acidification, the solvent was removed *in vacuo* and the residue was extracted with $CHCl_3$, dried ($MgSO_4$), and evaporated *in vacuo* to give 9.5 g (94%) of white solid, mp 118–120°. Recrystallization from pentane gave an analytical sample as white crystals: mp 118–120°; ir 3.70–4.00 (bonded OH), 5.92 μ (C=O); nmr τ 5.34 (s, 1, OH), 7.55 (br, 2, CH_2), 8.07–8.38 (s, 15H).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.05; H, 9.32.

***N*-Methyl-2-adamantaneacetamide (6).**—The reaction of 8.9 g (0.046 mol) of **4** with thionyl chloride gave 9.4 (97%) of the acid chloride **5**, ir 5.50 μ (C=O). It was dissolved in 50 ml of dry tetrahydrofuran (THF) and added dropwise to 10 ml of 40% aqueous solution of monomethylamine. The THF was evaporated *in vacuo*, and the residue was extracted with $CHCl_3$, dried ($MgSO_4$), and concentrated to give 7.9 g (86%) of **6** as a white solid, mp 142–149°. Crystallization from CH_3CN gave an analytical sample as white needles: mp 147–150°; ir 3.05–3.25 (NH), 6.02–6.12 μ (C=O); nmr τ 4.00–4.30 (br, 1, NH), 7.14–7.22 (d, 2, CH_2), 7.70 (br, 3, NCH_3), 8.05–8.40 (s, 15H).

Anal. Calcd for $C_{13}H_{21}NO$: C, 75.31; H, 10.21; N, 6.76. Found: C, 75.21; H, 10.15; N, 6.76.

***N*-Methyl-2-adamantaneethylamine (7).**—To a well-stirred suspension of 3.0 g of lithium aluminum hydride in 100 ml of dry THF cooled in ice, a solution of 7.4 g (0.36 mol) of **6** in 100 ml of dry THF was added dropwise. The reaction mixture was then refluxed overnight. Working up the reaction yielded 6.5 g (90%) of **7** as an oil: ir 3.00 μ (NH); nmr τ 4.30–4.55 (NH), 7.16–7.55, 8.08–8.45. The hydrochloride of **7** was crystallized from CH_3CN to give an analytical sample, mp >270°, ir 3.30–4.10 μ (NH_2^+ and CH).

Anal. Calcd for $C_{13}H_{23}N\cdot HCl$: C, 67.99; H, 10.53; N, 6.10. Found: C, 68.11; H, 10.81; N, 6.02.

1-Chloro-*N*-methyl-2-adamantaneethylamine (9).—A solution of 15.4 g (0.08 mol) of **7** in CH_2Cl_2 was stirred at room temperature with 200 ml of 5% NaOCl for 2 hr. The aqueous layer was removed, 200 ml of fresh NaOCl was added, and the mixture was stirred overnight at room temperature. The organic layer was separated, washed with water, dried ($MgSO_4$), and evaporated *in vacuo* to give 16.4 g (90%) of **8** as an oil. Compound **8** was dissolved in 190 ml of acid solution (16.7 ml of 95–98% H_2SO_4, 4.3 ml of H_2O, and 160 ml of CH_3CO_2H) and photolyzed at 25° in a Hanovia photochemical reactor with a low-pressure mercury lamp. After 1 hr exposure, the reaction mixture gave a negative halogen test with KI solution. After cooling, the solution was made basic with 10% NaOH, extracted with $CHCl_3$, washed with water, dried ($MgSO_4$), and evaporated *in vacuo* to give 15.5 g (85%) of **9** as a yellow oil: ir 2.85–3.20 μ (NH); nmr τ 6.05–6.30 (br, 1, NH), 7.44–7.58 (m, 2, $CH_2N<$), 7.75–7.87 (d, 3, CH_3NH), 7.87–8.5 (br, 2, CH_2), 8.09–8.5 (s, 14 H). The hydrochloride of **9** was crystallized from CH_3CN to give an analytical sample, mp >270°.

Anal. Calcd for $C_{13}H_{22}NCl\cdot HCl$: C, 59.10; H, 8.77; N, 5.31. Found: C, 59.23; H, 8.92; N, 5.13.

1-Methyladamantano[1,2-*b*]pyrrolidine (10).—Compound **9** (4.5 g, 0.02 mol) was heated under nitrogen at 290° (previously heated oil bath) for 10 min. After cooling, the residue, ir 3.70–4.4 μ (N^+H-), was triturated with 10% NaOH. The oil that formed was extracted with $CHCl_3$, washed with water, dried ($MgSO_4$), and evaporated to give 3.2 g of residue. It was dissolved in 20 ml of acetic anhydride and stirred overnight at room temperature. The excess acetic anhydride was removed *in vacuo* and the residue was partitioned between $CHCl_3$ and 5 *N* HCl. The aqueous layer was separated, basified, extracted with $CHCl_3$, dried ($MgSO_4$), and evaporated *in vacuo* to give 1.3 g (34%) of **10** as a pale yellow oil. The hydrochloride of **10** was crystallized from dioxane to give white crystals: mp 231–236°; ir 3.70–4.44 μ ($>N^+H-$); nmr τ −2.17 to −1.50 (br, 1, N^+H), 5.83–6.42 (m, 2, $CH_2N<$), 6.90–7.30 (m, 2, CH_2), 7.35–7.45 (d, **3**, $>N^+HCH_3$), 7.65–8.5 (m, 14 H); mass spectrum m/e 191 ($M^+ - HCl$).

Anal. Calcd for $C_{13}H_{21}N\cdot HCl$: C, 68.55; H, 9.74; N, 6.15; Cl, 15.57. Found: C, 68.30; H, 9.61; N, 6.18; Cl, 15.38.

Registry No.—**3**, 25220-07-9; **4**, 26082-22-4; **6**, 32132-60-8; **7** HCl, 32132-61-9; **9** HCl, 32132-63-1; **10**, 32139-10-9.

Reevaluation of α-Alkyl Substituent Kinetic Effects on Acid- and Base-Catalyzed Enolization

JACQUES-EMILE DUBOIS,* PIERRE ALCAIS,
RAYMOND BROUILLARD, AND JEAN TOULLEC

*Laboratoire de Chimie Organique Physique de
l'Université de Paris VII associé au C.N.R.S., 75-, Paris 5°, France*

Received April 12, 1971

Recently published work indicates that a controversy still exists regarding the exact nature of the influence exerted by α-alkyl groups on the rates of enolization of carbonyl compounds. According to Warkentin, *et al.*,[1] "the usual effect of an α-alkyl substituent is to accelerate acid-catalyzed enolization and to retard base-catalyzed enolization relative to the corresponding rates for unsubstituted ketone." This statement appears to be well authenticated for the case of base-catalyzed enolization[1,2] but appears to be less definite for acid-catalyzed enolization.[3] The above generalization arises essentially from studies of the preferential enolization rates of ketones containing two reaction sites, which of course constitutes a slightly different problem from that encountered in the comparative studies of alkyl- and nonalkyl-substituted ketones. Actually this generalization is in contradiction with results obtained for phenyl alkyl ketones[4] and dialkyl

---

(1) (a) J. Warkentin and O. S. Tee, *J. Amer. Chem. Soc.*, **88**, 5540 (1966); (b) J. Warkentin and C. Barnett, *ibid.*, **90**, 4629 (1968).

(2) (a) D. P. Evans and J. J. Gordon, *J. Chem. Soc.*, 1434 (1938); (b) C. F. Cullis and M. S. Hasmi, *ibid.*, 2512 (1956); (c) C. Rappe, *Acta Chem. Scand.*, **20**, 2236 (1966).

(3) (a) H. M. E. Cardwell and A. E. H. Kilner, *J. Chem. Soc.*, 2430 (1951); H. M. Dawson and R. Wheatley, *ibid.*, 2048 (1910); H. M. Dawson and H. Ark, *ibid.*, 1740 (1911); (b) C. Rappe and W. H. Sachs, *J. Org. Chem.*, **32**, 3700 (1967), and references cited therein.

(4) D. P. Evans, *J. Chem. Soc.*, 785 (1936).

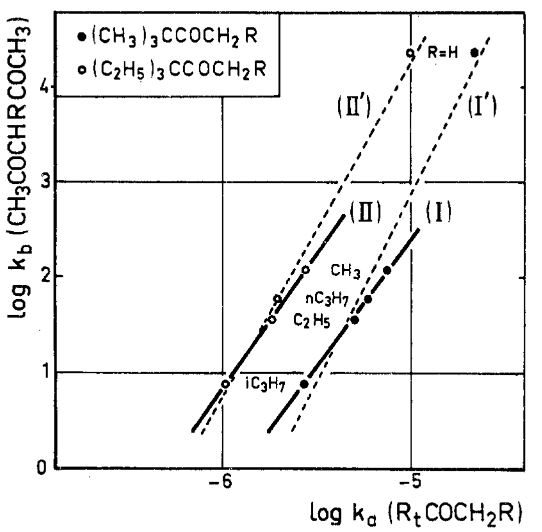


Figure 1.—Similar α-alkyl effects on acid- (k_a) and base- (k_b) catalyzed rate constants: with R = H (I'), $\log k_b = 22.7 + 3.96 \log k_a$ ($r = 0.983$); (II'), $\log k_b = 22.2 + 3.57 \log k_a$ ($r = 0.995$); without R = H (I), $\log k_b = 16.0 + 2.71 \log k_a$ ($r = 0.997$); (II), $\log k_b = 18.0 + 2.86 \log k_a$ ($r = 0.998$).

ketones[5,6] possessing a single enolization site, as well as with the results of the variation of the overall enolization rate of some dialkyl ketones with two different enolization sites.[7] Bothner-By and Sun,[8] on their part, maintain that α-alkyl substitution diminishes the acid-catalyzed reaction rate.

Our study of the acid-catalyzed enolization of R_tCOCH_2R (R_t = Me_3C or Et_3C) and of the base-catalyzed enolization of the diketone $CH_3COCHRCOCH_3$ allows a new approach to the latter problem. The results of these experiments are shown in Table I.

TABLE I

ACID- (MONOKETONES[a]) AND BASE- (β-DIKETONES[b]) CATALYZED ENOLIZATION RATE CONSTANTS

Compd R	$10^5 k_a$ (R_tCOCH_2R), sec^{-1} R_t = Me_3C[c]	 R_t = Et_3C	k_b $(CH_3COCHRCOCH_3)$, M^{-1} sec^{-1}
H	2.10	0.97	2.4×10^4 [d]
Me	0.72	0.27	130
Et	0.49	0.18	38
n-Pr	0.59	0.20	63
i-Pr	0.26	0.10	8

[a] Measurements were done at 25° in the following mixture: AcOH–H_2O (75% v/v), [HBr] = 0.5 *M*. Reproducibility ±5%. [b] At 25°, aqueoussolution, catalysis OH^-, ionic strength 0.1. Reproducibility ±10%. [c] See ref 6. [d] 4×10^4 M^{-1} sec^{-1} has also been measured; see M. Eigen, *Pure Appl. Chem.*, 6, 97 (1963); M. Ahrens, M. Eigen, W. Kruse, and G. Maass, *Ber. Bunsenges. Phys. Chem.*, 74, 380 (1970).

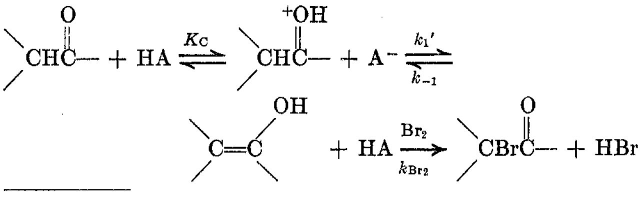
When the logarithms of the acid-catalyzed enolization rate constants, k_a, for a ketone with a given alkyl substituent R, are plotted against the logarithms of the base-catalyzed enolization rate constants k_b, for the β-diketones with the same alkyl substituent, straight lines are obtained (Figure 1). As is shown by the following diagram, the same correlations can be made between the rate constants found in the present study and those found in the literature for substituted alkyl phenyl ketones.[2a,4]

$$\begin{tikzcd}[column sep=large, row sep=large]
\log k_a\,(Me_3CCOCH_2R) \arrow[r, leftrightarrow, "\text{slope} = 2.71", "r = 0.997\ R \neq H"'] \arrow[d, leftrightarrow, "\text{slope} = 1.05"', "r = 0.994"] & \log k_b\,(CH_3COCHRCOCH_3) \arrow[d, leftrightarrow, "\text{slope} = 2.88"', "r = 0.997"] \\
\log k_a\,(C_6H_5COCH_2R) \arrow[r, leftrightarrow, "\text{slope} = 1.10", "r = 0.996,\ R \neq H"'] & \log k_b\,(C_6H_5COCH_2R)
\end{tikzcd}$$

It should be noted that the decrease in the rate constant observed in the presence of an α-alkyl substituent seems to be a general trend both for base- and acid-catalyzed reactions. *Furthermore, the decrease in the rate constant as a function of R (R ≠ H), is of the same magnitude both for acid and basic catalysis in the case of monoketones.*

These findings are somewhat surprising when one considers that it is generally admitted that the transition state for enolization under basic conditions is intermediate between the ketone and the enolate anion, whereas under acidic conditions the transition state is intermediate between the hydroxycarbonium ion and the enol.[9] The effects of structure and solvent on the rate of enolization have been explained on the basis of the charge distribution and structure in these transition states.[10] It seems doubtful that a given alkyl group would have the same effect, either polar or hyperconjugative, on transition states of opposite charges and differing structures. We will presently investigate our results supposing that (a) *dominant isosteric* influence of the R groups acts on the transition states of both acid- and base-catalyzed enolization, or (b) the substituents influence *primarily* the common ground state and have relatively little effect on the energy levels of the transition states.

In order to evaluate these hypotheses, it was necessary to have more information about the enol equilibrium constant. Such data are available from the studies carried out under acidic conditions at very low bromine concentrations.[6,11] Under these conditions, the successive steps of enolization and bromination have comparable rates. The well-known mechanism for this reaction can be represented as



---

(5) D. P. Evans and J. R. Young, *J. Chem. Soc.*, 1314 (1954).

(6) J. E. Dubois and J. Toullec, *Chem. Commun.*, 292 (1969).

(7) For an example, see P. D. Bartlett and C. H. Stauffer, *J. Amer. Chem. Soc.*, **57**, 2580 (1935).

(8) A. A. Bothner-By and C. Sun, *J. Org. Chem.*, **32**, 492 (1967).

(9) On the basis of experiments concerning kinetic isotopic substitution effects and the influence of catalysts (Brønsted correlations), it is accepted that the transition state is close to the enolate anion for the enolization of acetone ($\beta \cong 0.8$) by weak bases, midway between the ketone and the enolate anion for OH^-, and midway between the hydroxy carbonium ion and the enol for acid catalysis: C. G. Swain and A. S. Rosenberg, *J. Amer. Chem. Soc.*, **83**, 2154 (1961). This latter affirmation has been confirmed by a study of the solvent isotope effect on the conversion of 2-hydroxypropene into acetone under acidic conditions ($\alpha \cong 0.5$): J. E. Dubois and J. Toullec, *Chem. Commun.*, 478 (1969).

(10) The opposite effect of substituents on acid-catalyzed enolization ($\rho < 0$) and base-catalyzed enolization ($\rho > 0$) of aryl-substituted acetophenones and phenyl benzyl ketones is considered as one of the best pieces of evidence in favor of opposite charges in the transition states for acid and basic catalysis: A. Fischer, J. Packer, and J. Vaughan, *J. Chem. Soc.*, 3318 (1962); 226 (1963); D. P. Evans, V. G. Morgan, and H. B. Watson, *ibid.*, 1167 (1935); J. R. Jones, R. E. Marks, and S. C. Subba Rao, *Trans. Faraday Soc.*, **63**, 111, 993 (1967); H. J. Den Hertog and J. Koojman, *J. Catal.*, **6**, 347 (1966); S. Mishra, P. L. Nayak, and M. K. Rout, *J. Indian Chem. Soc.*, **46**, 645 (1969); D. N. Nanda, P. L. Nayak, and M. K. Pont, *Indian J. Chem.*, **7**, 469 (1969).

(11) J. E. Dubois and J. Toullec, *J. Chim. Phys.*, **65**, 2166 (1968).

If a quasistationary state is assumed for the enol, the rate equation may be written as

$$-\frac{\mathrm{d}[\mathrm{Br_2}]}{\mathrm{d}t} = \frac{[\mathrm{Br_2}]}{\dfrac{1}{k_{\mathrm{II}}[\mathrm{C}]} + \dfrac{1}{k_{\mathrm{a}}[\mathrm{C}]}[\mathrm{Br_2}]} \qquad \mathrm{(I)}$$

$$k_{\mathrm{a}} = K_{\mathrm{C}}k_1'[\mathrm{HA}] \qquad \mathrm{(II)}$$

$$k_{\mathrm{II}} = K_{\mathrm{E}}k_{\mathrm{Br_2}} = (K_{\mathrm{C}}k_1'/k_{-1})k_{\mathrm{Br_2}} \qquad \mathrm{(III)}$$

with the keto–enol equilbrium constant represented by K_{E}.

This being so, we have posited that, by analogy with the reactivity of α- and β-alkyl vinyl ethers,[12] the bromination rate constant $k_{\mathrm{Br_2}}$ is insensitive to variations in the structures studied.[13] In this case, the variations in the experimental bromination rate constant k_{II} follow those of the enol equilibrium constant K_{E}. It is extremely interesting in such conditions to look for a linear free-energy relation between k_{II} and k_{a}. Figure 2 indicates a very satisfying one with *unit slope* for ketones with *the same degree of α substitution.*

This highly significant direct correlation could be explained by assuming that the steric structural effects (hypothesis a) arise from the change in hybridization of the carbon α acting in the *same* manner on the energy of the transition state and on that of the enol; the unit slope observed for the alkyl-substituted ketones (R $\neq$ H) would then mean that the transition state is near the enol structure, *i.e.*, the hybridization change is almost completed. Unfortunately, such a conclusion cannot be drawn if one considers the proton is equally bonded to the hydroxycarbonium ion and the base and, therefore, not fully transferred.[9]

Steric effects for acid and base catalysis could also arise from interactions between the alkyl substituent and the base removing the proton in the slow step. *Such specific steric effects* on the transition state do not explain the parallelism between the rate constants and equilibrium constants for acid-catalyzed enolization.

On the other hand, the hypothesis that structural effects (R $\neq$ H) play a dominant role before the slow step in the reaction mechanism seems sufficient to explain the unit slope correlation between log k_{a} and log K_{E}. These effects can be determinant for the magnitude of the K_{C} stability (*cf.* eq II and III). However, this explanation as such cannot really account for the parallel substituent effects on the acid- and base-catalyzed reaction rates, except when the K_{C} variations *primarily* depend on the *ketone stability*. Interpretation b explaining these structural parallel effects then agrees with the unit slope rate–equilibrium relationship.

Such an analysis is still not fully satisfactory, since it implies a weak structural influence on the stability of the conjugated acid of the ketone, neglecting in particular solvation variations.[14] Moreover, it is highly probable[1a] that the population of conformers favorable to elimination is one of the major factors in determining the enolization rate. We are currently examining this aspect which could confirm our hypothesis regarding a dominant effect of alkyl groups before the slow step (conformational preequilibria).[15]

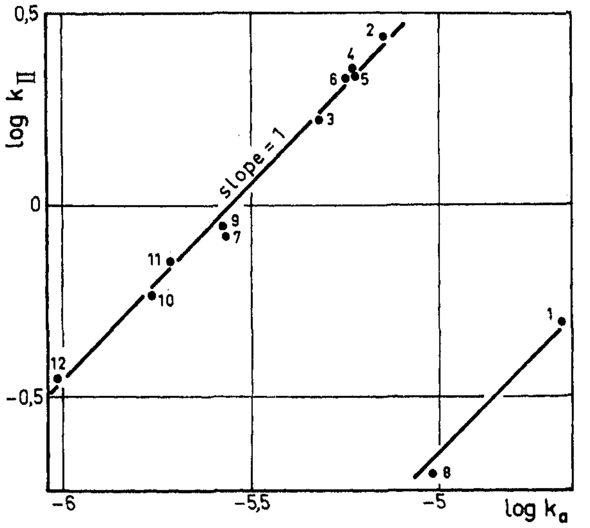


Figure 2.—Parallel structural effects on the bromination rate constants of $\mathrm{R_tCOCH_2R}$ (acid-catalyzed rate constant for enolization k_{a}, and apparent rate constant $k_{\mathrm{II}} = K_{\mathrm{E}}k_{\mathrm{Br_2}}$, for the bromination of the enol): **1**, $\mathrm{R_t}$ = $\mathrm{Me_3C}$, R = H; **2**, $\mathrm{Me_3C}$, Me; **3**, $\mathrm{Me_3C}$, Et; **4**, $\mathrm{Me_3C}$, *n*-Pr; **5**, $\mathrm{Me_3C}$, *n*-Bu; **6**, $\mathrm{Me_3C}$, *n*-pentyl; **7**, $\mathrm{Me_3C}$, *i*-Pr; **8**, $\mathrm{Et_3C}$, H; **9**, $\mathrm{Et_3C}$, Me, **10**, $\mathrm{Et_3C}$, Et; **11**, $\mathrm{Et_3C}$, *n*-Pr; **12**, $\mathrm{Et_3C}$, *i*-Pr.

Experimental Section

Solvents and Reagents.—The monoketones, which were synthesized as part of a general study of hindered ketones,[16] have been the object of a systematic study by ir[17] and uv[18] spectroscopy. Analysis by vpc has shown them to be consistently better than 99% pure. The β-diketones were commercially available compounds (K & K Laboratories) and were also purified by vpc to better than 99% purity. Their physical constants, ir spectra (Perkin-Elmer 225), and nmr spectra (Jeol JNM-C-60HL) were in accordance with those reported in the literature.

For the acid-catalyzed enolization of the monoketones, the solvent (0.5 *N* HBr in 75% v/v aqueous acetic acid) was prepared as follows: 25 ml of 2 *N* HBr (prepared from Merck "suprapur") was mixed with 75 ml of pure acetic acid (Merck "pro analysi," 99–100%) and the volume was brought to 100 ml by the addition of water distilled from $\mathrm{KMnO_4}$. For the base-catalyzed enolization of the β-diketones, the solvent used was a 0.1 *N* solution of $\mathrm{NaClO_4}$ in deionized water, the desired pH being obtained by the addition of 1 *N* NaOH.

Kinetic Measurements.—The acid-catalyzed rate constants, k_{a}, were obtained by the automated couloamperometric technique[19] which allows rapid changes in very low bromine concentrations to be followed. With this technique the ketone is always in large excess (*ca.* 10^{-2} *M*) with respect to the initial bromine concentration (10^{-4} to 10^{-6} *M* depending on the ketone). The two constants k_{a} and k_{II}'are calculated from the experimental data using an integrated form of the rate expression I.[6,11]

The base-catalyzed rate constants, k_{b}, were obtained by a chemical relaxation technique using a Messanlagen Studiengesellschaft (Göttingen, Germany) temperature-jump transient spectrometer (Type SBA7, Ser. No. 2-30). The calculation of the constant k_{b} from the experimental data has been described by Eigen in the case of the 2,4-pentanedione.[20]

---

(12) J. E. Dubois, J. Toullec, and G. Barbier, *Tetrahedron Lett.*, 4485 (1970).

(13) Supplementary evidence in favor of this supposition will be found in a later paper.

(14) The vapor-phase keto–enol equilibrium constant of α-alkyl keto esters shows the same dependency on the basic enolization rate constant k_{b} [J. B. Conant and A. F. Thompson, *J. Amer. Chem. Soc.*, **54**, 4039 (1932)], thus indicating that structural effects do not depend on the solvation of the various species.

(15) J. Toullec and J. E. Dubois, to be submitted for publication.

(16) J. E. Dubois, M. Chastrette, and E. Schunk, *Bull. Soc. Chim. Fr.*, 2011 (1967); J. E. Dubois, B. Leheup, F. Hennequin, and P. Bauer, *ibid.*, 1150 (1967); J. E. Dubois, G. Schutz, and J. M. Normant, *ibid.*, 3578 (1966).

(17) J. E. Dubois, A. Massat, and Ph. Guillaume, *J. Mol. Struct.*, **4**, 403 (1969); unpublished work.

(18) J. E. Dubois and A. Barbi, *J. Chim. Phys.*, **65**, 376 (1968); unpublished work.

(19) J. E. Dubois, P. Alcais, and G. Barbier, *J. Electroanal. Chem.*, **8**, 359 (1964).

(20) M. Eigen, *Pure Appl. Chem.*, **6**, 97 (1963); M. Ahrens, M. Eigen, W. Kruse, and G. Maass, *Ber. Bunsenges. Phys. Chem.*, **74**, 380 (1970).

Registry No.—**1**, 75-97-8; **2**, 564-04-5; **3**, 5405-79-8; **4**, 19078-97-8; **5**, 5340-64-7; **6**, 22921-92-2; **7**, 14705-50-7; **8**, 17535-47-6; **9**, 17535-48-7; **10**, 17535-49-8; **11**, 18295-58-4; **12**, 31938-27-9; $CH_3COCH_2COCH_3$, 123-54-6; $CH_3COCH(CH_3)COCH_3$, 815-57-6; CH_3CO-$CH(Et)COCH_3$, 1540-34-7; $CH_3COCH(n\text{-}Pr)COCH_3$, 1540-35-8; $CH_3COCH(i\text{-}Pr)COCH_3$, 1540-3-81.

Acknowledgment.—The authors wish to thank Professor K. Yates for his helpful discussions and comments.

Photodimerization of 4-Thiapyrone

Nobuyuki Ishibe* and Masao Odani

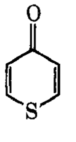
Department of Chemistry, Kyoto Institute of Technology, Matsugasaki, Kyoto 606, Japan

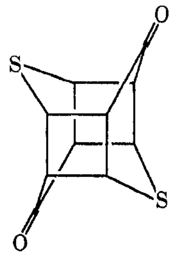
Received March 3, 1971

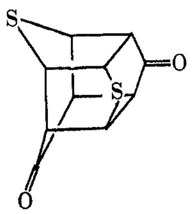
The photodimerization of unsaturated six-membered ring ketones which bear a heteroatom has been studied extensively. The structure of these photodimers depends upon the fragments of a polyene system which participate in a photoreaction. [2 + 2] cycloaddition products are obtained from 2-coumarins,[1] 2,3-dihydro-2,6-dimethyl-4-pyrone,[2] 2-pyrone,[3] and 2,6-diphenyl-4-thiapyrone;[4] [4 + 4] cycloaddition products from 4,6-dimethyl-2-pyrone[3] and 2-pyridones;[5] [2 + 2 + 2 + 2] cycloaddition products from 2,6-dimethyl-4-pyrone[6] and 2,6-dimethyl-4-thiapyrone.[7]

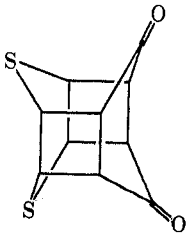
The present study is an attempt to extend these observations to 4-thiapyrone (I). The result on the photodimerization of I is reported here.

The irradiation of a 1% acetonitrile solution of I under nitrogen in a quartz tube with a medium-pressure lamp gave a photodimer, 3,9-dithiapentacyclo[6.4.-$0.0^{2,7}.0^{4,11}.0^{5,10}$]dodecane-6,12-dione (II). The structure of II was determined from the following spectral data. An examination of its nmr spectrum showed a multiplet at δ 3.45–3.70 assigned to the four α-carbonyl protons and a second multiplet at δ 4.55–4.80 ascribed to the four α-sulfide protons. There was no absorption attributable to an olefinic proton. The photoproduct no longer showed uv absorption characteristic of an unsaturated ketone. The infrared spectrum of the photoproduct has a strong carbonyl absorption at 1710 cm^{-1} and lacks other significant absorption in the 1650–1750-cm^{-1} region. The mass spectrum of the photoproduct displays a parent peak at *m/e* 224, which suggests that the photoproduct is a dimer of I. Moreover, the molecular weight determined by vapor pressure osmometry was 212, which was consistent with a dimeric species. From these results the alternative structures III and IV, in addition to II, could be written for this photodimer. Of these, III can be eliminated since there was no ir absorption of the carbonyl group in the five-membered ring (1745 cm^{-1}).[8] In the mass spectrum of the photodimer, the presence of a peak at *m/e* 112 corresponding to the ion of 4-thiapyrone, $(C_5H_4SO)^+$, and the absence of peaks at *m/e* 116 and 108 corresponding to the ions of 1,4-dithiacyclohexadiene, $(C_4H_4S_2)^+$, and 1,4-benzoquinone, $(C_6H_4O_2)^+$, respectively, suggest that the photodimer is assigned to the "head-to-tail" structure (II). Moreover, this assignment is confirmed from the fact that in addition to the peak of monomer I, an intense peak at *m/e* 86 was observed which may arise from I by expulsion of acetylene,[9] while the fragments at *m/e* 82, 80, and 54 were not observed, which could be expected from 1,4-benzoquinone ion.[10] These results indicate that the photoproduct has the structure II.


I


II


III


IV

While the irradiation of I in dioxane (2% solution) gave II in 2% yield, II was obtained in very low yield (<1%) from the irradiation of a 2% methanol solution of I. The 10% acetonitrile solution of I did not increase the yield of II. The photoreaction of I sensitized by benzophenone resulted in formation of II in 2% yield. This result suggests that the photodimerization of I proceeds *via* the excited triplet state of I.

The photodimerization of I leads exclusively to the head-to-tail [2 + 2 + 2 + 2] cycloadduct in striking contrast to 2,6-diphenyl-4-thiapyrone[4] and in close analogy with 2,6-dimethyl- and 2,6-diethyl-4-pyrone[6,11] and 2,6-dimethyl-4-thiapyrone.[7] The presence of the phenyl group in the thiapyrone could increase the steric barrier to [2 + 2 + 2 + 2] cycloaddition. At the same time this could affect the nature of the excitation

---

[1] C. H. Krauch, S. Faird, and G. O. Schenck, *Chem. Ber.*, **91**, 625 (1966); G. S. Hammond, C. A. Stout, and A. A. Lamola, *J. Amer. Chem. Soc.*, **86**, 3103 (1964).

[2] P. Yates and D. J. McGeor, *Tetrahedron Lett.*, 455 (1969).

[3] P. de Mayo and R. W. Yip, *Proc. Chem. Soc.*, 84 (1964); W. H. Pirkle and L. H. Mckendry, *J. Amer. Chem. Soc.*, **91**, 1179 (1969); C. T. Bedford, J. M. Forrester, and T. Money, *Can. J. Chem.*, **48**, 2645 (1970); J. P. Guthrie, C. L. McIntosh, and P. de Mayo, *ibid.*, **48**, 237 (1970).

[4] N. Sugiyama, Y. Sato, H. Kataoka, C. Kashima, and K. Yamada, *Bull. Chem. Soc. Jap.*, **42**, 3005 (1969).

[5] E. C. Taylor and R. O. Kan, *J. Amer. Chem. Soc.*, **85**, 776 (1963); L. A. Paquette and G. Slomp, *ibid.*, **85**, 765 (1963).

[6] P. Yates and M. J. Jorenson, *ibid.*, **80**, 6150 (1958); *ibid.*, **85**, 2956 (1963).

[7] N. Sugiyama Y. Sato, N. Kashima, and K. Yamada, *Bull. Chem. Soc. Jap.*, **43**, 3205 (1970).

[8] K. Nakanishi, "IR Absorption Spectroscopy," Nankodo, Tokyo, 1960, p 48.

[9] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco Calif., 1967, p 208.

[10] Reference 13, p 527.

[11] P. Yates and E. S. Hand, *J. Amer. Chem. Soc.*, **91**, 4749 (1969), and the previous papers.