peroxide or *t*-butyl perbenzoate has been attributed to inductive effects.[9] In both cases the products, benzoate or phenyl radicals, are not significantly stabilized by resonance involving the ring, and the Hammett equation gives a low negative ρ-value (*e.g.*, for benzoyl peroxide, ρ is -0.38). More recently Bartlett and Hiatt[13] have shown that one driving force for the decomposition of peresters is the resonance stabilization of the free radical formed.

In the case of unsubstituted *t*-butyl N-phenylperoxycarbamates the decomposition is most probably controlled by resonance stabilization. Pedersen[12] has reported that *t*-butyl N-ethylperoxycarbamate is extremely stable. The decomposition of *t*-butyl N-α-napthylperoxycarbamate[3] was found in this Laboratory to be very rapid, while the N,N-diphenyl compound was too reactive to be prepared. The stability trend, ethyl > phenyl > α-naphthyl, seems to be that of increased resonance stabilization of the amino radical (not that of inductive control), and supports the picture of loss of carbon dioxide accompanying homolytic peroxide cleavage.[13]

If this scheme is accepted, then the accelerating effect of electron-releasing substituents and the corresponding retarding effect of electron-attracting substituents (ρ is -2.18) can be rationalized on the basis that the imino group ($-\ddot{N}H$) is much more electronegative than the peroxycarbamido group.

$$\left(-\ddot{N}H\overset{\overset{O}{\|}}{C}O_2R'\right)$$

Electron drift toward the nitrogen, aiding the formation of the anilino radical, would be increased by electron releasing substituents and decreased by electron attracting ones. (Note that in the present work N-*p*-tolyl- and N-p-anisylperoxycarbamates could not be prepared, presumably because of their ease of decomposition.)

In the N-*p*-nitroanilino radical the nitro group is apparently exerting two opposing effects. The polar effect, of withdrawing electrons from the ring, destabilizes the radical. However, as the nitro group can also bear the odd electron, there is added some small resonance stabilization. The result of these effects on the rates of decomposition of ring-substituted *t*-butyl N-phenylperoxycarbamates is: unsubstituted > *p*-nitro > *m*-nitro. On the Hammett plots (Figs. 1 and 2), the *p*-nitro compound is above the line, *i.e.*, it decomposes faster than predicted from the rates of other compounds in which the substituent cannot bear the odd-electron.

The present data are not sufficient for a complete separation of resonance, inductive and steric effects.

BROOKLYN 1, N. Y.

(13) P. D. Bartlett and R. R. Hiatt, THIS JOURNAL, **80**, 1398 (1958).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE UNIVERSITY]

Bis-(β-diketones). IV. dissociation Constants of Some Bis-(β-diketones)

BY DEAN F. MARTIN[1] AND W. CONARD FERNELIUS

RECEIVED SEPTEMBER 22, 1958

The acid dissociation constants of five bis-(β-diketones) of the type $RCOCH_2CO-Y-COCH_2COR$ in a mixed solvent of 75 volume per cent. dioxane and 25 volume per cent. water were measured (or estimated). The fifteen bis-(β-diketones) of the types $[(RCO)(R'CO)CH]_2CHR''$ and $(RCO)(R'CO)CH-Y-CH(COR)(COR')$ are so much weaker acids that it was necessary to determine their constants in a more polar enivronment of 50 volume per cent. dioxane and 50 volume per cent. water to keep the titration curve within the range of a *p*H meter. Some correlations of the pK_D values and structural features of the bis-(β-diketones) are presented.

Introduction

In continuation of a study of the synthesis and properties of bis-(β-diketones)[2-5] the acid dissociation constants of a number of bis-(β-diketones) have been determined. Although several investigations have been concerned with the determination of the dissociation constants of β diketones,[6-10] there seems to be but one study of bis-(β-diketones)[2] which reports the dissociation constants of several compounds of the type $RCOCH_2CO-Y-COCH_2COR$. There are reported here the dissociation constants of representative bis-(β-diketones) of the types $RCOCH_2CO-Y-COCH_2COR$, $[(RCO)(R'CO)CH]_2CHR''$ and $(RCO)(R'CO)CH-Y-CH(COR)(COR')$.

Experimental

Potentiometric Titrations.—The synthesis and properties of the bis-(β-diketones) used in this investigation are described elsewhere.[3-5]

The acid dissociation constants of the bis-(β-diketones) in water–dioxane mixtures containing 75 or 50 volumes per cent. dioxane at 30° were determined by a method described previously[7] using tetramethylammonium hydroxide at the base. Due to the closeness of the first and second

(1) Department of Chemistry, University College, London.

(2) E. H. Holst, Doctoral Dissertation, The Pennsylvania State University, Aug., 1955.

(3) D. F. Martin, M. Shamma and W. C. Fernelius, THIS JOURNAL, **80**, 4891 (1958).

(4) D. F. Martin, M. Shamma and W. C. Fernelius, *ibid.*, **80**, 5851 (1958).

(5) D. F. Martin, W. C. Fernelius and M. Shamma, *ibid.*, **81**, 130 (1959).

(6) M. Calvin and K. W. Wilson, *ibid.*, **67**, 2003 (1945).

(7) L. G. Van Uitert, *et al.*, *ibid.*, **75**, 451, 455 (1953); **76**, 5887 (1954).

(8) R. M. Izatt, *et al.*, *J. Phys. Chem.*, **58**, 1113 (1954); **59**, 80, 170, 235 (1955).

(9) D. M. Ericson and W. C. Fernelius, AEC Document, NYO-7711, May, 1956.

(10) W. G. Bordiun and G. S. Hammond, "Substituent Effects on the Spectra and Ionization Constants of Diaroylmethanes," U. S. Atomic Energy Commission, Oak Ridge, Tenn., (1954).

dissociation constants, it was expedient to determine their values by solution of simultaneous equations.[11]

The dissociation constants of azelyldiacetophenone could not be determined in the 75 per cent. dioxane solution because the compound could be titrated only to the neutralization of one of the two acidic hydrogens in the molecule. The compound was insoluble in 50 per cent. dioxane. However, a value of 13.1 was estimated for pK_{D_1}, the negative logarithm of the first acid dissociation constant (75% dioxane) from the relationship between the pK_{D_1}, pK_{D_2} values and the pH meter reading, B, as shown in Fig. 1.

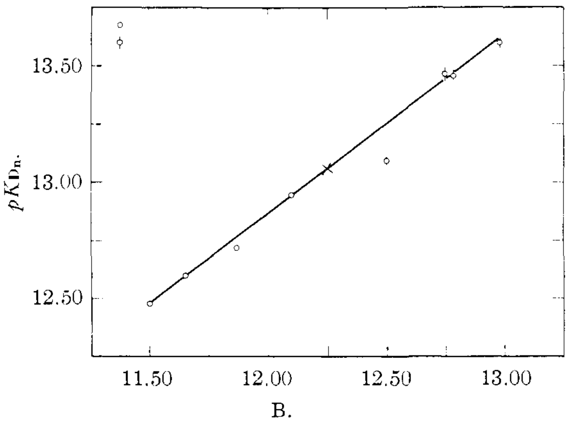


Fig. 1.—Relationship of pK_{D_n} and pH-meter B reading (B) at $^1/_4$ and $^3/_4$ neutralization of bis-(β-diketones) $RCOCH_2CO$—Y—$COCH_2COR$ in 75 vol. % dioxane at 30°; × represents the point corresponding to azelyldiacetophenone; O, pK_{D_1}, B $^1/_4$; ϕ, pK_{D_2}, B, $^3/_4$.

In this figure are plotted the pK_{D_1} and pK_{D_2} values as a function of the pH meter reading at $^1/_4$ (half neutralization of the first acidic hydrogen) and $^3/_4$ (half neutralization of the second acidic hydrogen) neutralization of the bis-(β-diketones), $RCOCH_2CO(CH_2)_nCOCH_2COR$.

TABLE I

pK_D VALUES OF BIS-(β-DIKETONES) OF THE TYPE $RCOCH_2$ CO-Y-$COCH_2COR$ IN 75 VOLUME PER CENT. DIOXANE SOLUTION (N_2 = 0.380) AT 30°

R	Y	pK_{D_1}	pK_{D_2}	Δ^a
C_6H_5	$(CH_2)_4$	12.47	13.09	0.62
C_6H_5	$(CH_2)_5$	12.72	13.46	.74
C_6H_5	$(CH_2)_6$	12.60	13.47	.87
C_6H_5	$(CH_2)_7$	13.1 (est.)	...	..
C_6H_5[b]	$(CH_2)_8$	12.58	13.69	1.11
CH_3[b]	$(CH_2)_8$	12.29	13.00	0.71
CH_2=$CH(CH_2)_2$	$(CH_2)_8$	12.95	13.60	.65
C_6H_5[b]	1,4-C_6H_4	11.34	12.30	.96
Acetylacetone[c]		12.70		
Benzoylacetone[c]		12.85		

[a] $\Delta = (pK_{D_2}) - (pK_{D_2})$. [b] Ref. 2. [c] L. G. Van Uitert, *et al.*, THIS JOURNAL, **75**, 455 (1953).

Discussion

Bis(β-diketones) of the type $RCOCH_2CO$-Y-$COCH_2COR$ are apparently inherently stronger acids than are the branched types $[(RCO)(R'CO)CH]_2CHR''$ and $(RCO)(R'CO)CH$-Y-$CH(COR)(COR')$. This is evidenced by the fact that the dissociation constants of the branched bis-(β-diketones) are too low to be determined in the 75 volume per cent. dioxane solution. The lower acidity of the branched bis-(β-diketones) is probably related to the fact that the two β-diketone functions are substituted on the active methylene position. A similar effect is noted with simple β-diketones: the pK_D of acetylacetone (10.35)[7] in 50% dioxane is less than that of n-butyl-2,4-pentanedione (12.07).[12]

In a general way, the relative acidities of the linear and branched bis-(β-diketones) can be related to their relative tendency to exist in the enolic form in the solid state. Thus the linear bis-(β-diketones) which exist largely in the enolic form in the solid state[13] are stronger acids than the branched bis-(β-diketones) which have a much lesser tendency to exist in the enolic form in the solid state.[14]

In the series $C_6H_5COCH_2CO(CH_2)_nCOCH_2COC_6H_5$ (n = 4–8), it is interesting to note that the pK_{D_1}, but not the pK_{D_2}, values show an alternation with chain length, n. The dissociation of the first proton occurs less readily for pimelyl-(n = 5) than for adipyl-(n = 4), suberyl-(n = 6) or sebacoyl-diacetophenone-(n = 8), and even less readily for azelyl-(n = 7) than for pimelyl-diacetophenone. The difference between the values of pK_{D_1} and pK_{D_2} appears to increase linearly as the chain length increases from 4 to 8. Unfortunately, it was not possible to obtain a value of pK_{D_2} for azelyldiacetophenone.

The fact that the second proton of the linear bis-(β-diketones) dissociates with increasing difficulty with increasing chain length is contrary to the behavior expected on the basis of distance of charge separation. By way of contrast, with compounds of the type $(CH_3CO)_2CH(CH_2)_nCH(COCH_3)_2$, the dissociation of the second proton apparently occurs more readily with increasing chain length. Thus the difference between the pK_{D_1}, pK_{D_2} values from 4.11 (n = 0) to 0.49 (n = 6) to 0.06 (n = 10).

The pK_D values of bis-(β-diketones)of the type $[(RCO)(R'CO)CH]_2CHR''$ are listed in Table II. For a given R'' group, the acetylacetone derivatives (R = R' = CH_3) have lower pK_{D_1} values than do the derivatives of methoxyacetylacetone (R = CH_3, R' = CH_3OCH_2). This result is interesting because acetylacetone has a higher pK_D than does methoxyacetylacetone (10.35 and 9.66, respectively, in 50% dioxane). Furthermore, on the basis of the inductive effect of the methoxyl group, the methoxyacetylacetone derivatives would be expected to be weaker acids than the acetylacetone derivatives. However, Dr. M. Shamma has suggested and models confirm that the ether oxygen from one of the CH_3OCH_2COCH=$C(OH)CH_3$ groups may be bonded by the same hydrogen which is chelated between the carbonyl and enol portions

(11) B. P. Block and G. H. McIntyre, Jr., THIS JOURNAL, **75**, 5667 (1953).

(12) B. B. Martin, M.S. Thesis, The Pennsylvania State University, January, 1959.

(13) This is evidenced[3] by the presence of hydroxyl absorption near 2.95 μ, strong enol-chelate absorption near 6.2–6.25 μ, and a general absence of normal carbonyl absorption.

(14) This is evidenced[4,5] by the strong carbonyl absorption in the 5.75–5.9 μ region and weak to moderate enol-chelate absorption near 6.2 μ.

TABLE II

pK_D VALUES OF BIS-(β-DIKETONES) OF THE TYPE $[(RCO)(R'CO)CH]_2CHR''$ IN 50 VOLUME PER CENT. DIOXANE SOLUTION (N_2 = 0.175) AT 30°

R	R'	R''	pK_{D_1}	pK_{D_2}	Δ^a
CH_3	CH_3	$(CH_2)_5CH_3$	11.33	12.52	1.19
CH_3	CH_3	C_6H_5	11.10	12.49	1.39
CH_3	CH_3	$2\text{-}ClC_6H_4$	11.04	12.73	1.69
CH_3	CH_3	$2\text{-}C_5H_4N$	9.80	12.46	2.66
CH_3	CH_3	$2\text{-}CH_3OC_6H_4$	11.47	12.44	0.97
CH_3	CH_3	$3,4\text{-}CH_2O_2C_6H_3$	11.39	12.60	1.21
CH_3	CH_3	$3\text{-}C_5H_4N$	10.29	12.63	2.34
CH_3	CH_3	$4\text{-}CH_3OC_6H_4$	11.62	12.61	0.99
CH_3	CH_3	$4\text{-}(CH_3)_2NC_6H_4$	11.50	12 45	.95
CH_3	CH_3OCH_2	C_6H_5	11.54	12.27	.63
CH_3	CH_3OCH_2	$2\text{-}C_5H_4N$	10 95	12.49	1.54
CH_3	CH_3OCH_2	$4\text{-}(CH_3)_2NC_6H_4$	12.13	12.31	0.18
CH_3	CH_3OCH_2	$4\text{-}CH_3OC_6H_4$	11.74	12.49	0.75
	$CH_3OCH_2COCH_2COCH_3$		9.66[b]		
	$(CH_3CO)_2CH(CH_2)_3CH_3$		12.07[c]		

[a] $\Delta = (pK_{D_2}) - (pK_{D_1})$. [b] Ref. 9. [c] Ref. 12.

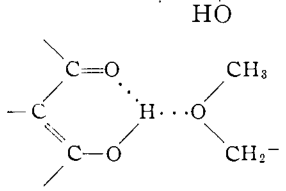
TABLE III

pK_D VALUES OF BIS-(β-DIKETONES) OF THE TYPE (RCO)-(R'CO)CH–Y–CH(COR)(COR') IN 50 VOLUME PER CENT. DIOXANE SOLUTION (N_2 = 0.175) AT 30°

R	R'	Y	pK_{D_1}	pK_{D_2}	Δ^a
CH_3[b]	CH_3		9.43	13.54	4.11
CH_3	CH_3	$(CH_2)_6$[c]	11.99	12.48	0.49
CH_3	CH_3	$(CH_2)_{10}$	12 01	12.07	.06
CH_3	CH_3	$1,4\text{-}(CH_2)_2C_6H_4$	11 27	12.15	.88

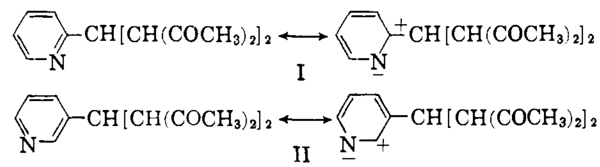
[a] $\Delta = (pK_{D_2})\text{-}(pK_{D_1})$. [b] Ref. 2. [c] β-Form.[5]

of the other $CH_3OCH_2COCH{=}CCH_3$ group
HO



The effect of the third oxygen would be to lower the availability of the proton or to increase the pK_D.

The nature of the R'' group of bis-(β-diketones) of the type $[(RCO)(R'CO)CH]_2CHR''$ has a marked influence on the pK_D values. For example, two acetylacetone derivatives (R = R' = CH_3) for which R'' is 2-pyridyl or 3-pyridyl have markedly low pK_{D_1} values; the 3-pyridyl derivative is a weaker acid than the 2-pyridyl. This is attributed to the resonance of the 2-pyridyl compound I which would tend to withdraw electrons inductively resulting in the higher acidity of the tetraketone. On the other hand, the resonance forms of the 3-pyridyl compound II are such that the inductive effect is reduced.[15]



A number of the bis-(β-diketones) listed in Table II contain R'' groups which are substituted phenyl groups. It is possible to relate the nature of the substituent and the pK_{D_1} value of the bis-(β-diketone). For example, the compound for which R = R' = CH_3 and R'' = $4\text{-}CH_3OC_6H_4$ has a higher pK_{D_1} value than does the compound for which R'' = C_6H_5 (11.62, 11.10, respectively). This is attributed to the activating influence of the methoxy group. The resulting increase in the electron density on the carbon atom alpha to the methylene groups would tend to make the proton more difficult to remove. The effect of other electron-withdrawing substituents can be similarly rationalized.

Acknowledgment.—The authors gratefully acknowledge financial support furnished for this work by the United States Atomic Energy Commission through Contract AT(30-1-)-907.

UNIVERSITY PARK, PENNA.

(15) The effect of a pyridyl group on pK_D values is also seen in the series $RCOCH_2COCH_3$, for which pK_D values (50 volume per cent. dioxane) of 10.45 (R = C_6H_5), 10.37 (R = CH_3), 9.72 ($2\text{-}C_5H_4N$) and 8.83 ($4\text{-}C_5H_4N$) are reported.[7]