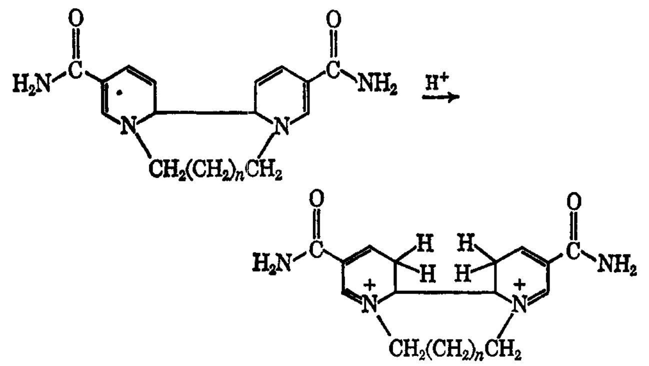

mined by differences in energies of double bonds exocyclic to rings of various sizes.

Workers in the field of pyridine chemistry will recognize the difficulties in the classical approach of isolating and characterizing compounds of intermediate oxidation state such as described here. Physical evidence like ultraviolet and esr spectra must be relied upon heavily. Obviously, the most convincing test of the present scheme would involve the unequivocal synthesis of the carbamido-substituted "Diquat" IX and a study of the radical obtained upon its reduction. Unhappily, attempts to prepare IX by a synthetic route independent of the work reported here have so far been unsuccessful.

Registry No.—II, $n = 0$, 19293-83-5; II, $n = 1$, 19293-84-6; I, $n = 2$, 19293-85-7; II, $n = 3$, 19293-86-8.

Acknowledgments.—The authors are deeply grateful to Professors David J. Goldsmith, Leon Mandell, and Peter Pappas for their interest in this work and for many helpful discussions.

Application of the Hammett Equation to Nonaromatic Unsaturated Systems. VII. Heterovinylene Sets

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Ionization constants for 10 heterovinylene sets have been correlated with the extended Hammett equation $Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + h$. Sets studied include disubstituted oximes, disubstituted glyoximes, *syn-* and *anti*-substituted aldoximes, substituted acetyl oximes, substituted methyl oximes, *syn-* and *anti*-substituted phenyl oximes, substituted phenylimines, and substituted ethoxyimines. Good results were generally obtained. The magnitude of α is dependent upon molecular geometry. Assignment of configuration by means of correlation with the Hammett equation is discussed.

In previous papers of this series we have considered the application of the Hammett equation[1] to *trans*-[2] and *cis*-vinylene,[3] vinylidene,[4] and heterovinylidene[4] sets. Our purpose in this paper is to extend these studies to include *cis*- and *trans*-heterovinylene sets. Two types of heterovinylene sets have been investigated: (1) oximes, in which the reaction site is the hydroxyl group bonded to the nitrogen atom; (2) imines, in which the reaction site is a full nonbonding orbital on the nitrogen atom.

Ionization constants for oximes and imines taken from the literature have been correlated with the extended Hammett equation

$$Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + h \qquad (1)$$

by multiple linear regression analysis. The data used in the correlations are given in Table I. The σ_I constants were taken from our collection;[5] the σ_R constants were obtained from

$$\sigma_R = \sigma_p - \sigma_I \qquad (2)$$

The σ_p constants were from the compilation of McDaniel and Brown.[6] In some cases values of σ were taken from previous papers in this series or were estimated by our method.[7]

The justification for the correlation of the ionization constants (as pK_a values) of the disubstituted oximes (set 1) with eq 1 is as follows. The effect of the substituent may be written

$$Q_X = \alpha_{syn}\sigma_{I,X^1} + \alpha_{anti}\sigma_{I,X^2} + \beta_{syn}\sigma_{R,X^1} + \beta_{anti}\sigma_{R,X^2} + h \qquad (3)$$

As $X^1 \equiv X^2$, eq 3 becomes

$$Q_X = (\alpha_{syn} + \alpha_{anti})\sigma_{I,X} + (\beta_{syn} + \beta_{anti})\sigma_{R,X} \qquad (4)$$

equivalent to eq 1 with

$$\alpha = \alpha_{syn} + \alpha_{anti}, \qquad \beta = \alpha_{syn} + \beta_{anti}$$

The correlation of the *anti*-disubstituted glyoximes II with eq 1 may be justified in the same manner. The

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[1] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953); R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y. 1956, p 565; V. Palm, *Russ. Chem. Rev.* (Eng. Transl.) **31**,, 471 (1961); P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).

[2] M. Charton and H. Meislich, *J. Amer. Chem. Soc.*, **80**, 5940 (1958); M. Charton, *J. Org. Chem.*, **30**, 552 (1965).

[3] M. Charton, *ibid.*, **30**, 974 (1965).

[4] M. Charton, *ibid.*, **30**, 557 (1965).

[5] M. Charton, *ibid.*, **29**, 1222 (1964).

[6] D. H. McDaniel and H. C. Brown, *ibid.*, **23**, 420 (1958).

[7] M. Charton, *ibid.*, **28**, 3121 (1963).

TABLE I
DATA USED IN CORRELATIONS

1. Ionization constants of $X_2C{=}NOH$ in water at 25°

X	Me	Et	Ph	Ac	CF_3
pK_a	12.42	12.60	11.18	7.38	6.0
Ref	*a*	*a*	*b*	*c*	*d*

2. Ionization constants of $(XC{=}NOH)_2$ in water at 25°

X	H	Cl	Me	NH_2	Et	Pr	2-Furyl
pK_a	9.02	2.94	10.72	10.62	10.67	10.81	9.80
Ref	*e*	*e*	*e*	*f*	*g*	*g*	*h*

3. Ionization constants of *syn* aldoximes in water at 25°

X	$3\text{-}C_6H_4NO_2$	$4\text{-}C_6H_4NO_2$	$4\text{-}C_6H_4NMe_2$	2-Furyl	Ph	$4\text{-}C_6H_4OMe$	t-PhC_2H_2	CF_3
pK_a	10.16	9.96	11.25	10.85	10.68	10.92	10.55	8.9
Ref	*i*	*i*	*i*	*i*	*j*	*j*	*j*	*d*

4. Ionization constants of *anti* aldoximes in water at 25°

X	Ph	$3\text{-}C_6H_4NO_2$	*t*-PhC_2H_2	2-Furyl	2-thienyl	*n*-C_6H_{14}
pK_a	11.33	10.74	10.80	11.16	10.76	11.60
Ref	*j*	*j*	*j*	*k*	*k*	*j*

5. Ionization constants[c] of $XAcC{=}NOH$ in water at 25°

X	H	Me	Et	*i*-Pr	Ac	CO_2Et[e]
pK_a	8.30	9.30	9.38	9.50	7.38	7.07

6. Ionization constants of $XMeC{=}NOH$ in water at 25°

X	Me	Et	Ph	Ac	NO_2
pK_a	12.42	12.45	11.35	9.30	7.4
Ref	*a*	*a*	*b*	*c*	*m*

7. Ionization constants of *syn*-phenyl ketoximes in water at 25°

X	$4\text{-}O_2NC_6H_4$	Ph	H
pK_a	10.47	11.18	11.33
Ref	*i*	*b*	*j*

8. Ionization constants of *anti*-phenyl ketoximes in water at 25°

X	$4\text{-}O_2NC_6H_4$	Ph	H	Me
pK_a	10.85	11.18	10.68	11.35
Ref	*i*	*c*	*j*	*c*

9. Ionization constants of $XPhC{=}NH_2^+Cl^-$ in water at 25°

X	MeS	EtS	PhS	MeO	EtO	Ph	NH_2
pK_a	5.85	6.049	4.481	5.68	6.37	7.00	11.9
Ref	*n*	*n*	*n*	*o*	*p*	*q*	*r*

10. Half-neutralization potentials of $X(OEt)C{=}NH_2^+$ in $MeNO_2$[s]

X	Ph	Me	EtO_2CCH_2	CCl_3	$4\text{-}O_2NC_6H_4$
HNP	308	198	385	770	441

11. Ionization constants[t] of α-substituted tetronic acids in water at 25°

X	H	Cl	Br	I	Me	Et	CO_2Me	Ac	NO_2	Ph	*i*-$PrCH_2CH_2$
pK_a	3.76	2.13	2.23	2.31	4.19	4.00	1.80	1.80	1.68	3.69	4.16

12. Ionization constants[u] of 3-substituted 2-hydroxy-1,4-naphthoquinones in water at 26–33°

X	H	Bz	Ph	$PhCH_2$	*i*-$PrCH_2CH_2$	*t*-$MeCH{=}CH$
pK_a	4.00	2.17	4.35	4.90	5.13	4.8

13. Ionization constants[v] of 3-substituted 1-aza[2.2.2]bicyclo-2-octanes in water at 25°

X	H	Ph	$CONH_2$	CO_2Me	CN
pK_a	10.95	10.23	9.67	9.40	7.81

14. Second ionization constants[w] of 3-substituted 4-pyridones in water at 20°

X	H	CO_2NH_2	CN	NO_2
pK_{a_2}	10.5	9.3	7.35	7.0

15. Second ionization constants[x] of 5-substituted 2-pyridones in water at 20°

X	H	Me	Cl	I	Br	NO_2
pK_{a_2}	11.70	12.01	9.87	9.93	10.03	7.97

16. Second ionization constants[x] of 3-substituted 2-pyridones in water at 20°

X	H	Me	Cl	Br	NO_2
pK_{a_1}	11.70	12.59	10.40	10.42	8.52

[a] C. V. King and A. P. Marion, *J. Amer. Chem. Soc.*, **66,** 977 (1944). [b] C. Calzolari, *Univ. Studi Trieste. Fac. Sci., Inst. Chim.*, 4 (1954); *Chem. Abstr.*, **49,** 7338*d* (1954). [c] A. L. Green and B. Saville, *J. Chem. Soc.*, 3887 (1956). [d] B. L. Dyatkin, E. P. Mochalina, and I. L. Knunyants, *Tetrahedron,* **21,** 2991 (1965). [e] H. E. Ungnade, G. Fritz, and L. W. Kissinger, *ibid.*, **19,** *Suppl.* 1, 235 (1963). [f] H. E. Ungnade, L. W. Kissinger, A. Narath, and D. C. Barham, *J. Org. Chem.*, **28,** 134 (1963). [g] C. V. Banck and S. Anderson, *Inorg. Chem.*, **2,** 112 (1963). [h] V. M. Sarostina, E. K. Astrakhova, and V. M. Peshkova, *Vestn. Mosk. Univ., Ser. II Khim.*, 18 (2), 43 (1963). [i] O. L. Brady and N. M. Chekshi, *J. Chem. Soc.*, 946 (1929). [j] O. L. Brady and R. F. Goldstein, *ibid.*, 1918 (1926) [k] S. G. Tandon, *J. Phys. Chem.*, **65,** 1644 (1961). [l] P. T. Muller and E. Bauer, *ibid.*, **2,** 472 (1904). [m] J. Armand, *Bull. Soc. Chim. Fr.*, 882 (1966). At 21°. [n] R. H. Hartigan and J. B. Cloke, *J. Amer. Chem. Soc.*, **67,** 709 (1945). [o] J. Stieglitz, *Am. Chem. J.*, **39,** 29, 156 (1908). [p] E. S. Hand and W. P. Jencks, *J. Amer. Chem. Soc.*, **84,** 3505 (1962). [q] K. Koehler, W. Sandstrom, and E. H Cordes, *ibid.*, **86,** 2413 (1964). [r] A. Albert, R. Goldacre, and J. Phillips, *J. Chem. Soc.*, 2940 (1948). Includes statistical factor of ½. [s] C. A. Streuli, *Anal. Chem.*, **31,** 1652 (1959). HNP values are half-neutralization potentials. [t] L. J. Haynes and J. R. Plimmer, *Quart. Rev.*, **14,** 292 (1960). [u] M. G. Ettinger, *J. Amer. Chem. Soc.*, **72,** 3085 (1950). [v] C. A. Grob, *Chem. Ind.* (London), 598 (1957). [w] T. Wieland, C. Fest, and G. Pfleiderer, *Ann.*, **642** 163 (1961). [x] E. Spinner and J. C. B. White, *J. Chem. Soc., B*, 991 (1966).

TABLE II

RESULTS OF CORRELATIONS WITH EQ 1

Set	$-\alpha$	$-\beta$	h	R[a]	F[b]	r[c]	s_{estd}[d]	s_α[d]	s_β[d]	s_h[d]
1	11.5	4.53	11.55	0.997	196.7	0.864	0.305	1.45	1.97	0.247
2	15.9	3.39	9.66	0.990	98.21	0.288	0.493	1.13	0.806	0.241
2A	15.8	3.44	9.59	0.990	49.96	0.212	0.644	1.59	1.07	0.396
3	4.43	1.01	10.94	0.985	81.06	0.835	0.151	0.758	0.748	0.169
4	3.10	0.627	11.31	0.892	3.654	0.146	0.240	1.15	1.64	0.249
4A	3.41	0.923	11.37	0.946	8.439	0.166	0.171	0.831	1.17	0.203
5	3.28	2.89	8.80	0.950	13.95	0.683	0.359	0.725	1.05	0.176
6	5.95	3.19	11.73	0.9992	607.5	0.722	0.126	0.297	0.604	0.0818
8	−0.408	4.48	10.74	0.954	5.034	0.484	0.159	0.878	1.51	0.146
9	20.6	5.41	9.15	0.947	17.42	0.200	0.949	4.82	1.72	1.38
10	−1360	542	162	0.988	40.27	0.780	48.3	218.	678	78.2
11	3.61	1.79	3.61	0.955	41.28	0.159	0.350	0.434	0.783	0.156
11A	4.43	2.54	3.64	0.996	495.8	0.0653	0.0976	0.147	0.231	0.0436
12	3.84	6.27	4.18	0.992	90.79	0.767	0.179	1.10	1.11	0.141
13	5.75	−2.33	11.02	0.998	261.5	0.657	0.102	0.301	0.763	0.07895
14	5.91	−4.68	10.48	0.993	363.0	0.591	0.106	0.361	2.44	0.105
15	4.89	2.53	11.58	0.998	392.7	0.050	0.116	0.181	0.400	0.0868
16	4.54	2.95	11.85	0.997	180.1	0.059	0.162	0.254	0.558	0.122

Set	n[e]	C.L.[f]	t_α[g]	C.L.[h]	t_β[g]	C.L.[h]	t_h[g]	C.L.[h]
1	5	99.0	7.931	98.0	2.299	80.0	46.76	99.9
2	7	99.9	14.07	99.9	4.206	98.0	40.08	99.9
2A	5	97.5	9.930	99.0	3.229	90.0	24.20	99.0
3	8	99.9	5.844	99.0	1.350	50.0	64.73	99.9
4	6	<90.0	2.696	90.0	0.482	20.0	45.42	99.9
4A	5	<90.0	4.103	90.0	0.789	20.0	56.01	99.9
5	6	95.0	4.524	95.0	2.752	90.0	50.0	99.9
6	5	99.5	20.03	99.9	5.281	95.0	143.4	99.9
8	4	<90.0	0.465	20.0	2.967	50.0	73.56	99.0
9	7	97.5	4.274	98.0	3.145	95.0	6.630	99.0
10	5	97.5	6.239	95.0	0.799	20.0	2.072	80.0
11	11	99.9	8.318	99.9	2.286	90.0	23.14	99.9
11A	10	99.9	30.14	99.9	10.00	99.9	83.49	99.9
12	6	99.5	3.491	95.0	5.649	98.0	29.65	99.9
13	5	99.5	19.10	99.0	3.054	90.0	139.7	99.9
14	4	95.0	16.37	95.0	1.918	50.0	99.81	99.0
15	6	99.9	27.02	99.9	6.325	99.0	133.4	99.9
16	5	99.0	17.87	99.0	5.287	95.0	97.13	99.9

[a] Multiple correlation coefficient. [b] F test for significance of regression. [c] Partial correlation coefficient of σ_{I} on σ_{R}. [d] Standard errors of the estimate, α, β, and h, respectively. [e] Number of points in the set. [f] Confidence level for regression. [g] Student "t" test for significance of α, β, and h. [h] Confidence levels for α, β, and h.

effect of the substituent is given by

$$Q_{\mathrm{X}} = \alpha_{21}\sigma_{\mathrm{I,X}^1} + \alpha_{24}\sigma_{\mathrm{I,X}^2} + \alpha_{31}\sigma_{\mathrm{I,X}^2} + \alpha_{34}\sigma_{\mathrm{I,X}^2} + \beta_{21}\sigma_{\mathrm{R,X}^1} + \beta_{24}\sigma_{\mathrm{R,X}^1} + \beta_{31}\sigma_{\mathrm{R,X}^2} + \beta_{34}\sigma_{\mathrm{R,X}^2} + h \quad (5)$$

where

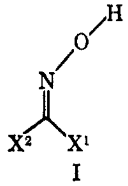
$$\alpha_{21} = \alpha_{34}, \qquad \alpha_{24} = \alpha_{31}, \qquad \beta_{21} = \beta_{24}, \qquad \beta_{24} = \beta_{31} \quad (6)$$

As $X^1 \equiv X^2$, we obtain

$$Q_{\mathrm{X}} = (2\alpha_{21} + 2\alpha_{24})\sigma_{\mathrm{I,X}} + (2\beta_{21} + 2\beta_{24})\sigma_{\mathrm{R,X}} + h \quad (7)$$

equivalent to eq 1 with

$$\alpha = 2\alpha_{21} + 2\alpha_{24}, \qquad \beta = 2\beta_{21} + 2\beta_{24} \quad (8)$$



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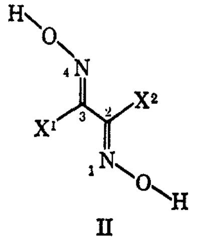

II

Results

The results of the correlations with eq 1 are presented in Table II. In some sets only three points were available and therefore correlation with eq 1 was not possible. In this event the data were correlated with the simple Hammett equation

$$Q_{\mathrm{X}} = \rho\sigma_{\mathrm{X}} + h \quad (9)$$

using the σ_{I}, σ_m, and σ_p constants. The σ_m constants were taken from McDaniel and Brown. The results of these correlations are given in Table III.

Oximes.—Very good results were obtained for the disubstituted oximes (set 1). The results for the disubstituted glyoximes (set 2) are significant at the 99.9% C.L., indicative of an excellent correlation. Excellent results were obtained for the *syn* aldoximes (set 3). Poor results were obtained for the correlation of the *anti* aldoximes (set 4); although the results are significantly improved by the exlusion of the value for X = *trans*-cinnamyl (set 4A), they are still not significant at the 90% C.L. Correlation of the data with the σ_{I} constants by means of eq 9 (set 4B, Table III)

TABLE III

RESULTS OF CORRELATIONS WITH EQ 9

Set	$-\rho$	h	r[a]	s[b]	s[b]	t[c]	n[d]	C.L.[e]
4B	3.30	11.45	0.928	0.159	0.765	4.317	5	95.0
7 I	3.98	11.42	0.953	0.196	1.26	3.152	3	80.0
m	4.02	11.37	0.995	0.0668	0.415	9.674	3	90.0
p	3.33	11.24	0.980	0.130	0.678	4.908	3	80.0
8A I	1.82	11.29	0.970	0.0878	0.459	3.969	3	80.0
m	1.74	11.25	0.993	0.0434	0.212	8.227	3	90.0
p	1.26	11.55	0.998	0.0248	0.0874	14.46	3	95.0
10A	1221	220	0.984	45.3	128	9.532	5	99.0

[a] Correlation coefficient. [b] Standard errors of the estimate and ρ, respectively. [c] Student "t" test for significance of the regression. [d] Number of points in set. [e] Confidence level.

TABLE IV

CALCULATED VALUES OF pK_a

Compound	pK_a Obsd	Calcd	Set	Δ	pK_a, calcd	Set	Δ
Acetyl aldoxime	8.30	9.4	3	1.1	10.5	4B	2.2
Benzoyl aldoxime	8.25	9.5	3	1.2	10.5	4B	2.2
Propionyl aldoxime	8.37	9.6	3	1.2	10.5	4B	2.1

gave fair results, however. Fair and excellent correlations, respectively, were obtained for the acetylketoximes (set 5) and methyl ketoximes (set 6).

Very poor results were obtained for the *anti*-phenyl ketoximes (set 8). Elimination of the value for X = H (set 8A) gave fair correlation with eq 9 using the σ_p constants. Correlation of the *syn*-phenyl ketoximes (set 7) with eq 9 gave best results with the σ_m constants. That the results are poor is probably due to the set containing only three points.

***cis*-Enols.**—For comparison we have correlated data for α-substituted tetronic acids (set 11) and for 3-substituted 2-hydroxy-1,4-naphthoquinones (set 12) with eq 1. Although excellent results were obtained for set 11, a great improvement results from the exclusion of the value for X = NO_2 (set 11A). The results obtained for set 12 were excellent.

Imines.—Good results were obtained both for the ionization constants of the substituted phenylimines (set 9) and the half-neutralization potentials of the substituted ethyl imidates (set 10). Correlation of the half-neutralization potentials with the σ_I constants by means of eq 9 gave very good results.

Enamines and Enamides.—It was desirable for purposes of comparison to examine data for *trans*-enols. As such data are unavailable, we have turned to the *trans*-enamines as an appropriate system for comparison. The results of the correlation of the 3-substituted 1-aza[2.2.2]bicyclo-2-octenes (set 13) are excellent. It must be noted, however, that the value of β is undoubtedly in error as it is opposite in sign to the value of α. A "t" test shows β to be statistically significant at the 90% C.L. The 95% C.L. for β is 2.33 ± 3.28 (or the range −0.95 to 5.63). Thus a negative value of β is quite possible.

Fair correlation was obtained for the 3-substituted 4-pyridones. Again the value of β was positive. In this case however, a "t" test shows that β is significant only at the 60% C.L. and may probably be disregarded. The 5- and 3-substituted 2-pyridones gave excellent and very good correlations respectively (sets 15 and 16).

Discussion

Stereochemistry.—The configuration of the oximes in sets 4 and 7 are known, as are all those of set 8 with the exception of acetophenone oxime, all those of set 3 with the exception of the trifluoroacetyl aldoxime, and all those of set 2 with the exception of diethyl and dipropyl glyoximes. As the values of α, β, and h for set 2A, which excluded diethyl and dipropyl glyoxime, are essentially the same as those obtained including these compounds (set 2), we conclude that these compounds have the *anti* configurations.

Inspection of models suggests that the substituted acetyl ketoximes (set 5) should have the *anti*-acetyl configurations. For acetyl aldoxime this is supported to some extent by a calculation of the pK_a of the *syn* and *anti* isomers from the correlations obtained for sets 3 and 4B, respectively. The results are shown in Table IV; the results for benzoylaldoxime and propionyl aldoxime are also presented in Table IV.

As the agreement between calculated and observed values is poor, and the uncertainty in α and β for set 4B is large, this evidence is not conclusive. The existence of the acyl aldoximes in a hydrogen-bonded *syn*-acyl configuration can be ruled out, as the hydrogen bond would decrease the predicted acid strength, which should result in a higher pK_a than that calculated for set 4B, rather than one which is lower by ~2.2 pK_a units. We believe, therefore, that the more likely configuration of the acyl aldoximes is the *anti*-acyl configuration.

Some support for the assignment of the *anti* configuration to acetyl methyl ketoximes (3-oximino-2-butanone) is obtained from the work of Lustig,[8] who reports that the nmr spectra of methylcarbonalkoxy ketoximes show that only one configuration is present, and suggests that this is the *syn*-methyl configuration.

In view of the closeness of the pK_a values of the ethyl and isopropyl acylketoximes to that for the methyl

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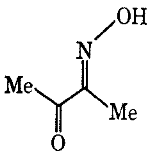
(8) E. Lustig, *J. Phys. Chem.*, **65**, 491 (1961).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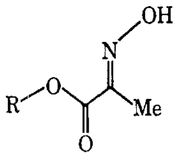
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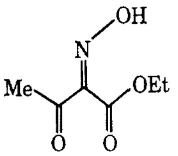
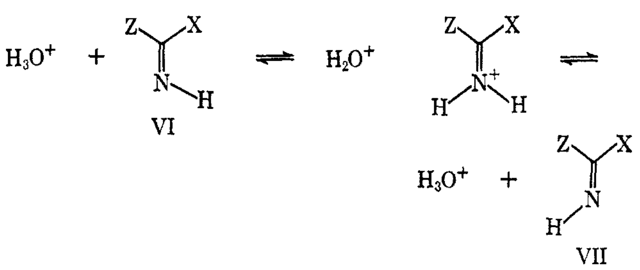

V

compound the configuration for all of the alkyl acetyl ketoximes should be the same. Thus all of the members of set 5 (X = H, Me, Et, *i*-Pr, Ac) ought to have an acetyl group *anti* to the OH group. The successful correlation of set 5 with eq 1 is a necessary but not sufficient condition for the identity of configuration. Thus, although good correlation was obtained for set 5, this does *not* constitute proof of the identity of configuration throughout the set. That inclusion of the value for X = CO_2Et does not result in any significant change in α, β, or h does suggest that both of the members of the set do indeed have the same configuration and that the configuration of ethyl α-oximinoacetoacetate (ethyl-2-oximino-3-butanonoate) is also the *anti*-acetyl configuration, V.

Lustig reports that acetophenone oxime exists as a pure stereoisomer. He states in a later paper[9] that in all of the cases he has studied the *syn*-methyl configuration predominates. It seems likely then that acetophenone oxime exists in the *syn*-methyl configuration. This conclusion is supported by the work of Karabatsos and Taller[10] who find that in CCl_4 acetophenone exists in the *syn*-methyl configuration to the extent of 94%. Reasons for believing the configuration of dimethylglyoxal monoxime to be *anti*-acetyl (this is identical with *syn*-methyl) were noted above. Lustig reports that methyl ethyl ketoxime exists as a mixutre of *syn* and *anti* forms. As he states that the *syn*-methyl form predominantes, and the pK_a observed for methyl ethyl ketoxime is in good agreement with that found for dimethyl ketoxime for which no stereoisomers are possible, it would seem that the observed pK_a is close to the pK_a of the *syn* isomer of methyl ethyl ketoxime. Thus we believe that in all of the members of set 6 the *syn*-methyl configuration predominates.

The assignment of the *syn* configuration to trifluoroacetyl aldoxime is based on the configurations of aldoximes reported by Karabatsos and Taller.[10] The results of these authors show that increasing bulk of the X group in XC(NOH)H favors the *syn* configuration. The trifluoromethyl group is considerably larger than a methyl group (the minimal prependicular van der Waals radii of the groups are 1.72 Me, and 2.11 CF_3).[11] This suggests that trifluoroacetyl aldoxime exists predominantly in the *syn* configuration.

The imines studied are capable of existing in two tautomeric forms, one in which substituent and proton are *syn* (VI), the other in which they are *anti* (VII). As the localized effect predominates in these sets and all of the substituents studied are acceptors by the localized effect, it seems likely that one of the two tautomers is predominant. At the present, no assignment of configuration to the predominant tautomer is possible.


VI

VII

The Magnitude of the Electrical Effect in Heterovinylene Sets.—As a measure of the magnitude of the electrical effect we may take the value of α or ρ. The values of α for oxime configurations in which the substituent and hydroxyl group are *syn* (sets 4B, 5, and 8A) are 3.30, 3.28, and 1.26, respectively. By comparison the values of α for the *cis*-enols (sets 11A and 12) are 4.43 and 3.84, respectively. Owing to there being only three points in set 8A, the uncertainty in its value of α is quite large. Thus no successful comparison can be made between the *cis*-enols and the *anti*-phenyl ketoximes. The α values obtained for the *cis*-enols are in fairly good agreement with those obtained for the *anti* aldoximes and the acetyl ketoximes. This is in accord with the concept that α values are determined predominantly by molecular geometry. For the oximes in which substituent and hydroxyl group are *anti* we may make comparisons with the *trans*-enamines. The values of α for the *syn* aldoximes (set 3), methyl ketoximes (set 6), and *syn*-phenyl ketoximes (set 7A) are 4.43, 5.95, and 4.02, respectively. For the 3-substituted 1-aza[2.2.2]bicyclo-2-octenes (set 13), 3-substituted 4-pyridones (set 14), and 5-substituted 2-pyridones (set 15) we observed α values of 5.75, 5.91, and 4.89. To correct for the difference between OH and NH acids, we multiply the average α value for the *trans*-enamines by the ratio of ρ for phenols to ρ for anilinium ions (the value of which is 0.76);[12] the result is 4.0. The results obtained for the *syn* aldoximes and *syn*-phenyl ketoximes are in good agreement with those for the *trans*-enamines. The value for methyl ketoximes seems too high. The sum of the average α values for *cis*-enols and that or the *trans*-enamines corrected as above should serve for comparison with the disubstituted oximes (set 1). The sum obtained is 8.2. The observed value of α for set 1 is about 11.5 which again seems somewhat high.

In the case of the disubstituted glyoximes (set 2), α_{24} may be estimated to be about that of the geometrically similar *cis*-3-substituted acrylic acids and related systems.[3] The ρ values for the *cis*-3-substituted acrylic and methacrylic acids and trans-3-methylacrylic acid are -2.34, -3.48, and -3.29, respectively. Using an average value of ρ of -3 and the value of ρ for 2-substituted acrylic acids as a model for α_{21} (the value is 4.25),[4] we may use eq 8 to calculate α for set 2. The calculated value of α is 14.5, in very good agreement with the observed value of 15.9.

The α value of the phenylimines (-20.0) may be compared with those of the C-substituted amidines, N-phenyl-O-substituted amidines, and the substituted methylamines for which the ρ values are -12.0, -12.1,

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[9] E. Lustig, unpublished results.

[10] G. J. Karabatsos and R. A. Taller, *Tetrahedron*, **24**, 3167 (1968).

[11] M. Charton, *J. Amer. Chem. Soc.*, **91**, 615 (1969).

[12] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

and −8.57. The α value observed for the imines is very much larger than might have been expected.

Although the results are by no means conclusive, they suggest that the *syn* oximes are less sensitive to substitutent effects than are the *anti* oximes. Apparently the substitution of nitrogen for carbon in a double bond does not affect the magnitude of the electrical effect.

Composition of the Electrical Effect.—The composition of the electrical effect may be described by ϵ where[13]

$$\epsilon = \beta/\alpha \qquad (10)$$

for correlations with eq 9, ϵ is determined by the type of substituent constant used in the calculation,

$$\sigma_X = \lambda\sigma_{I,X} + \delta\sigma_{R,X} \qquad (11)$$

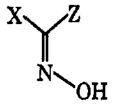
and

$$\epsilon = \delta/\lambda \qquad (12)$$

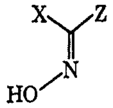
For the σ_m and σ_p constants the ϵ values are 0.33 and 1.00, respectively.

The three sets of oximes in which the substituent X has the *anti* configuration, VIII (sets 3, 6, and 7), have an average value of ϵ of 0.37. Thus these compounds can be correlated with eq 9 by means of the σ_m constants. In the case of those sets of oximes in which the substituent X has the *syn* configuration, IX, a value of ϵ of ~1 is observed for two of the sets, while for the third set ϵ is 0. We may compare these results with those of the *cis*-enols for which ϵ values of 0.56 and 1.5 are obtained. For the enamines and enamides the values of β are not good enough to permit a worthwhile comparison for sets 13 and 14. For sets 15 and 16 values of ϵ are 0.52 and 0.65, respectively.

For the substituted phenylimines a value of ϵ of 0.26 is obtained, while, for the substituted ethyl imidates, ϵ cannot be calculated owing to the uncertainty in β. The value obtained for the substituted phenylimines is in accord with the values observed for C-substituted and C-substituted N-phenylamidines.



VIII



IX

The Use of Correlatable Properties in the Assignment of Configuration.—Consider some property which may be correlated by eq 1 or eq 9. If data of this type for two sets differing in configuration is correlated-with either eq 1 or eq 9 three possible situations may conceivably arise: (1) all of the data lie on the same line; (2) the data lie on two parallel lines; (3) the data lie on two nonparallel lines.

The magnitude of α, and therefore of ρ, depends upon the molecular geometry of the system. Then unless the two configurations have equivalent geometries, cases 1 and 2 will not be realized. Thus when the two configurations are geometric isomers or diastereomers case 3 is the usual result. Some important properties of case 3 must be noted. If the correlation lines are not parallel they must intersect. This means that the correlated property for one configuration cannot always be greater than that for the other configuration. That configuration with greater values on one side of the point of intersection of the correlation lines must have smaller values on the other side. Thus if the correlatable property is to be used in the assignment of configuration, the correlation equations for both of the configurations must be known.

The utility of this method of configurational assignment must be a function of the difference between the slopes of the correlation lines and the location of the point of intersection. In most systems the unsubstituted compound (for which X = H) is a member of both sets and is therefore the point of intersection. The smaller the difference in the slopes of the correlation lines, the wider the region in which the two configurations will not differ sufficiently to permit distinction between configurations.

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(13) M. Charton, *J. Amer. Chem. Soc.*, **86**, 2033 (1964).