

***EZ* Isomerization of 2,4-Dinitrophenylhydrazones¹**

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The acid-catalysed *EZ* isomerization of a series of α -substituted acetophenone 2,4-dinitrophenylhydrazones has been investigated. In contrast to reports by other workers on similar systems, the isomerization is influenced not only by steric effects but by polar effects as well indicating that it is probably incorrect to neglect in general the influence of polar effects on isomerizations about the $-\text{C}=\text{N}-$ bond. The correlation of the first-order rate constants with structural parameters and the mechanism of the isomerization (*i.e.* lateral shift vs. internal rotation) are discussed.

THE most commonly encountered derivatives of carbonyl compounds are ones which contain the azomethine bond ($-\text{C}=\text{N}-$). Because of their usefulness in the characterization of carbonyl compounds, the 2,4-dinitrophenylhydrazones (DNP's) are probably the most familiar of these derivatives. The question of stereoisomerism and the factors which affect isomerization in DNP's have received attention from many workers. Of particular interest among these are Ramirez and Kirby's² u.v. and i.r. data for the *E* and *Z*-DNP's of alkyl phenyl ketones, Karabatsos and his co-workers'³

† For all the DNP's studied, the isomer initially subjected to the acid catalyst was always the one having the 2,4-dinitroanilino-group and the α -substituent on the same side of the $-\text{C}=\text{N}-$ bond.^{2,3} Thus the *EZ* process being followed was the same in each case.

¹ For a discussion on the application of the stereochemical terms *E* and *Z* see J. E. Blackwood, C. L. Gladys, K. L. Leoning, A. E. Petrarca, and J. E. Rush, *J. Amer. Chem. Soc.*, 1968, **90**, 509.

extensive n.m.r. studies on the DNP's of aliphatic and aliphatic-aromatic aldehydes and ketones and, Hegarty and Scott's⁴ rate studies of the *E* to *Z* isomerization which occurs during the bromination of alkylidene DNP's. These studies indicate that the only apparent structural parameters of importance which affect isomerization around the $-\text{C}=\text{N}-$ bond in these systems are of steric origin. We have investigated the acid-catalysed *EZ* isomerization (*i.e.* $E \rightleftharpoons Z$ or $Z \rightleftharpoons E$ depending on the particular DNP)† for a series of α -substituted acetophenone DNP's and have found that the influence of structural parameters on the first-order rate constants

² (a) F. Ramirez and A. F. Kirby, *J. Amer. Chem. Soc.*, 1953, **75**, 6026; (b) F. Ramirez and A. F. Kirby, *ibid.*, 1954, **76**, 1037; (c) L. E. Scoggins and C. K. Hancock, *J. Org. Chem.*, 1961, **26**, 3490.

³ G. J. Karabatsos, F. M. Vane, R. A. Taller, and N. Hsi, *J. Amer. Chem. Soc.*, 1964, **86**, 3351, plus earlier papers in this series cited therein.

⁴ A. F. Hegarty and F. L. Scott, *J. Org. Chem.*, 1968, **33**, 753.

for this isomerization can be described best only in terms of both steric and polar effects.

The rates of the *EZ* isomerization of the various DNP's to their respective equilibrium mixtures are shown in the Table. On inspection of these data, it is apparent

Rate constants for the acid-catalysed *EZ* isomerization of α -substituted acetophenone 2,4-dinitrophenylhydrazones (DNP) at 25° in chloroform

Compd.	X in DNP of PhCOX	$10^5 k/s^{-1}$
(1)	Me	1.170
(2)	Et	1.897
(3)	Pr ⁿ	5.795
(4)	n-C ₈ H ₁₁	1.811
(5)	n-C ₉ H ₁₉	2.580
(6)	Pr ⁱ	0.921
(7)	CH ₂ Cl	1.556
(8)	CH ₂ Br	1.645
(9)	CH ₂ I	1.795
(10)	CH ₂ OMe	3.940
(11)	CH ₂ NO ₂	0.582
(12)	CH ₂ CO ₂ Et	1.136
(13)	CH ₂ OAc	0.970
(14)	CH ₂ Ph	1.851
(15)	CH ₂ OPh	1.705
(16)	CH ₂ SMe	2.087

that no simple relation exists between the rates for all the DNP's and either the polar effects of the various α -substituents alone or the steric effects alone. For example, compound (9) reacted at about the same rate as compound (2) even though polar effects operate in opposite directions for the two compounds and steric effects are expected to be of greater importance for (9). The absence of any such simple relationships was confirmed by the very poor correlations obtained by linear regression analyses^{5a} of $\log k$ on σ^* ^{6a,7}, E_s ^{6b}, or E_s^c .⁸ However, using the extended Taft equation approach (*i.e.* $\log k = \log k_0 + \rho^* \sigma^* + \delta^c E_s^c$),^{6c} a fairly good multiple correlation was obtained between the $\log k$ values for all the compounds and both σ^* and E_s^c . That is, the multiple regression analysis^{5b} of $\log k$ on σ^* and E_s^c gave a ρ^* value of -0.05 and a δ^c of $+0.49$ with $R = 0.916$ and $s = 0.09$. This implies that both the polar and steric effects of the various α -substituents affect the isomerization with the steric effect, as indicated by the relative magnitude of δ^c compared to ρ^* , being the more important. It is interesting to note that in spite of significantly different reaction conditions, the δ^c value obtained in the present study ($+0.49$) is, as expected, more positive than the $\delta^c(+0.34)$ obtained from the correlation of Hegarty and Scott's rate constants⁴ † for the *E* to *Z* isomerization which occurs during the bromination of alkylidene DNP's. In their study, Hegarty and Scott found polar effects negligible

† The correlation of Hegarty and Scott's⁴ $\log k$ values with E_s^c was carried out in this laboratory and gave $r = 0.994$, $s = 0.03$, $\delta^c = +0.34$, and $\log k_0(\text{CH}_3) = -2.48$.

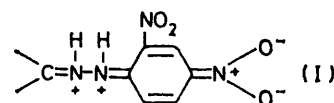
‡ The α -bromo-, -chloro-, -iodo-, -methoxy-, -nitro-, and -phenoxy-acetophenone DNP's were included.

⁵ G. W. Snedecor, 'Statistical Methods,' The Iowa State College Press, Ames, Iowa, 1956, 5th edn., (a) ch. 6; (b) ch. 14.

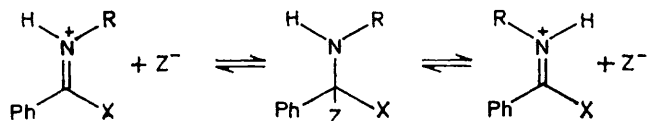
⁶ R. W. Taft, 'Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956, (a) p. 606; (b) p. 598; (c) p. 586.

and steric factors the only substituent effect of importance. While steric factors appear to be of greater magnitude for our series and are certainly the more important substituent effect, the influence of polar effects still cannot be ignored. This is implied by the described multiple-regression analysis and by the result of a linear-regression analysis of $\log k$ on σ^* for only those DNP's with very polar but relatively small steric substituents.† That is, a quite good correlation was obtained which gave a ρ^* of -0.90 with $r = 0.976$ and $s = 0.06$. Therefore, we feel that it is probably incorrect to neglect in general the influence of polar effects on isomerizations about the $-\text{C}=\text{N}-$ bond. This is particularly true for DNP's and related systems.

Even though polar effects cannot be ignored when considering the isomerization, steric factors are still the substituent effect of preponderant influence. This would seem to indicate that the isomerization does not take place through the lateral shift (or inversion) mechanism,^{9,10} since the transition state for such would have to draw some contribution from the highly improbable resonance structure (I). However, an internal



rotation mechanism, as suggested previously by Karabatsos,³ would account for the importance of both polar and steric effects. In addition, the inclusion of the



R = NH-2,4-Dinitrophenyl

anion of the catalytic acid in the isomerization step is in keeping with the observed faster isomerization of aldehyde DNP's as compared to ketone DNP's.³

EXPERIMENTAL

Materials.—The α -substituted acetophenones not available through commercial sources were prepared as reported previously in the literature. The DNP's were all prepared by Johnson's method¹¹ and their physical properties were found to agree satisfactorily with literature values. Spectroquality chloroform was used in all the rate studies.

Rate Measurements.—The procedure was identical for all the DNP's studied. A Beckman model DU-2 spectrophotometer was used to record the absorbances and follow the reactions. The constant temperature bath and the room in which the spectrophotometer was located were maintained at $25.0 \pm 0.5^\circ$.

⁷ P. R. Wells, 'Linear Free Energy Relationships,' Academic Press, Inc., New York, 1968, p. 38.

⁸ C. K. Hancock, E. A. Meyers, and B. J. Yager, *J. Amer. Chem. Soc.*, 1961, **83**, 4211.

⁹ D. Y. Curtin, E. J. Grubles, and C. G. McCarty, *J. Amer. Chem. Soc.*, 1966, **88**, 2775.

¹⁰ H. Kessler, *Angew. Chem. Internat. Edn.*, 1970, **9**, 219.

¹¹ G. D. Johnson, *J. Amer. Chem. Soc.*, 1951, **73**, 5888.

The following is a typical procedure: A 3×10^{-4} M-chloroform solution of the DNP was prepared in a 25 ml volumetric flask and placed in the constant-temperature bath for 48 h. At the end of that time, a 1.0 ml aliquot was pipetted into a 10 ml volumetric flask and diluted with chloroform to give a 3×10^{-5} M-solution. The absorbance (A_0) of this solution was then determined at the λ_{\max} of the DNP, at $\lambda_{\max} + 10$ nm, at $\lambda_{\max} - 10$ nm; the solution was then discarded. Conc. sulphuric acid (0.1 ml) was then added to the original stock solution which was then shaken for several minutes to ensure complete mixing; it was then placed back into the constant-temperature bath for thermal re-equilibration. Samples (1.0 ml) were pipetted at various intervals into a 10 ml volumetric flask and diluted with chloroform to give a 3×10^{-5} M-solution; the absorbance (A) was determined at λ_{\max} , $\lambda_{\max} + 10$ nm, and λ_{\max}

$- 10$ nm. This procedure was continued until the absorbance no longer changed. At this point the equilibrium absorbance (A_e) was recorded. The rate constant was then obtained from a linear plot¹² of $\ln (A_e - A_0)/(A_e - A)$ against time (t), the plot being determined by linear-regression analysis.^{5a} The rate constants determined at the different wavelengths were found to agree closely in all cases and the averages reported in the Table are the result of at least three determinations. The maximum deviation from the mean of replicate k values did not exceed 5%.

The rate constant calculations and the various correlations with σ^* and E_s^c were performed on an IBM 1130 computer.

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¹² A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism,' Wiley, New York, 1953, p. 172.