reagent characteristic as polarizability.[10] But we have not considered the physical nature of the special interaction of reagent with substrate.

Some of the most important forces of attraction between molecules not undergoing chemical reaction are those variously known as van der Waals or London or dispersion forces.[11] These forces are proportional to the product of the polarizabilities of the atoms concerned and inversely proportional to the seventh power of the distance between the atoms. London forces have an important influence on many physical properties. They are, for example, largely responsible for the greater solubility of iodine (I_2) and of stannic iodide in bromoalkane solvents than in corresponding chloroalkanes.[12,13]

One would expect London forces to contribute to the lowering of transition state energy and thus to an increase in reaction rate, when the transition state structure is such as to bring atoms of high polarizability close to one another. This would appear to be the nature of the effect with which this paper is concerned.[14]

It should be emphasized that the accelerative effect arising from the mutual interaction of substrate and reagent atoms of high polarizability does not mean that change from a substituent or reagent of low to one of high polarizability necessarily brings about an increase in reaction rate. The new substituent, for example, may have steric, inductive and/or mesomeric effects which depress the reaction rate. Examples can be found in Tables I, II and III. What it does mean is that after allowances have been made for these other factors, as we have done by considering suitable rate ratios, the change to a substituent of higher polarizability will have caused more acceleration, or less deceleration, the greater the effective polarizability of the nucleophilic reagent.

Assuming that the special characteristics in reagent and substrate are correctly identified as polarizabilities and that their special interaction is in the nature of London forces, we can expect that this factor exerts a significant influence in yet other classes of chemical reactions. It will be of interest to discover other manifestations of this effect.

It is a pleasure to acknowledge discussions with Drs. Herbert C. Brown and Will D. Merritt, Jr., which have been of great help in formulating the ideas set forth in this paper.

Chapel Hill, N. C.

---

[10] For many years, polarizability in a nucleophilic reagent has been considered to contribute substantially to nucleophilic reactivity and polarizability in a group being displaced has been considered to contribute substantially to displaceability. *Cf.* E. D. Hughes, *Trans. Faraday Soc.*, **34**, 195 (1938); G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 422; C. G. Swain and C. B. Scott, This Journal, **75**, 141 (1953). These views appear to be sound, but they should be clearly differentiated from the proposition that has been arrived at in this paper, namely, that the *special increase* in reactivity which attends the reaction of a reagent such as the iodide ion with a substrate having a large and heavy halogen atom at or near the site of substitution is due to the high polarizabilities of both reagent and halogen substituent. The *general* contribution of polarizability to nucleophilic reactivity is allowed for, and the *special* reagent characteristic is revealed, by comparison of substrate ratios such as the k_{RI}/k_{RBr} ratios in Table V.

[11] O. K. Rice, "Electronic Structure and Chemical Binding," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 354; J. R. Partington, "An Advanced Treatise on Physical Chemistry," Vol. I, Longmans, Green and Co., London, 1949, p. 741.

[12] J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd ed., Reinhold Publishing Corp., New York, N. Y., 1950, pp. 373 and 376.

[13] S. A. Shchukarev, L. S. Lilich and A. B. Sheinin, *Doklady Akad. Nauk S.S.S.R.*, **85**, 1333 (1952); *C. A.*, **47**, 383 (1953).

[14] There is one troublesome point concerning this interpretation. If the special interaction is indeed of the nature of London forces, it seems strange that bromine atoms in *m*- and *p*-bromobenzyl chlorides should still exert a significant influence on the iodide:hydroxide ratio (Table IV). London forces fall off extremely rapidly with distance. This point requires further consideration.

[Contribution from the Department of Research in Chemical Physics, Mellon Institute]

Spectral Evidence for Tautomerism in Diazo Ketones

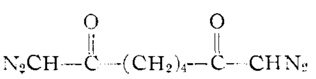
By Foil A. Miller and William B. White

Received June 10, 1957

Ultraviolet absorption of the group $N_2CH-CO-CH_2-$ varies considerably with change in solvent. In cyclohexane and dioxane there is a single intense band near 247 mμ; in water and acetic acid this band is weaker, and another intense one appears near 275 mμ. Seven other solvents gave intermediate results. In mixtures of water and acetonitrile of varying composition there is a smooth transition from the one case to the other. The resulting family of curves goes through an approximate isosbestic point, which suggests an equilibrium between two forms. Two such equilibria were considered: a keto–enol tautomerism and a diazo–isodiazo tautomerism. Although the results are not conclusive, infrared measurements of the intensities of the diazo and the carbonyl bands support the latter. It may be represented as $\overset{-}{N}=\overset{+}{N}=CH-CO- \rightleftarrows HN=\overset{+}{N}=\overset{-}{C}-CO-$

Introduction

Ultraviolet absorption is useful in studying diazo ketones because the group $N_2-CH-CO-$ has a characteristic band at 245–250 mμ.[1] Although changing the solvent usually has only a minor effect on the absorption spectrum, Morgan, Renfrew and Moore[2] discovered that the electronic spectrum of 1,8-bisdiazo-2,7-octanedione (I) depends markedly



$$N_2CH-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_4-\overset{\overset{\displaystyle O}{\|}}{C}-CHN_2$$

I

---

[1] (a) S. A. Fusari, *et al.*, This Journal, **76**, 2878 (1954); (b) S. A. Fusari, T. H. Haskell, R. P. Frohardt and Q. R. Bartz, *ibid.*, **76**, 2881 (1954).

[2] M. S. Morgan, A. G. Renfrew and A. M. Moore, paper presented at 129th Meeting of Amer. Chem. Soc., Dallas, Tex., April, 1956.

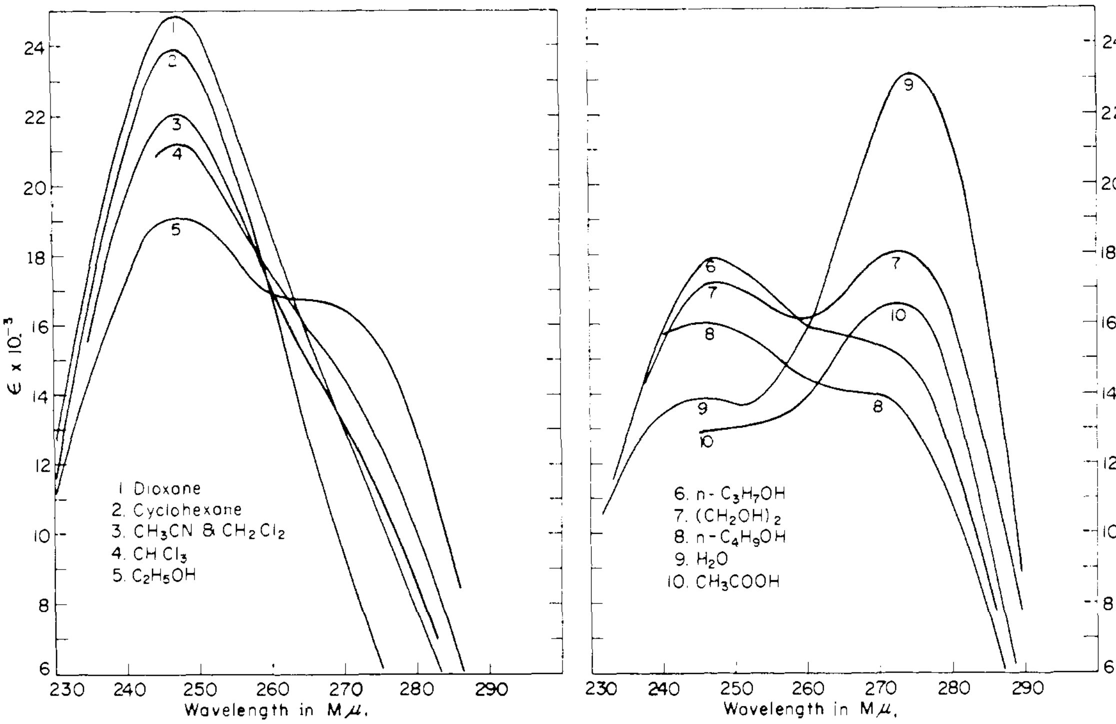


Fig. 1.—Ultraviolet spectrum of 1,8-bisdiazo-2,7-octanedione (I) in various solvents, $\epsilon = (1/bc) \log_{10} (I_0/I)$ (l./mole cm.): 1, dioxane; 2, cyclohexane; 3, acetonitrile, methylene chloride; 4, chloroform; 5, ethanol; 6, *n*-propyl alcohol; 7, ethylene glycol; 8, *n*-butyl alcohol; 9, water; 10, glacial acetic acid.

on the solvent in which it is measured.[3] The present study was an effort to learn more about the nature and cause of this interesting effect.

Results

Figure 1 shows the ultraviolet absorption of I in a variety of solvents. Many of these curves are taken from the paper by Morgan and co-workers.[2] Table I lists the wave lengths and intensities of the band maxima for all the compounds studied in this work. In general in solvents containing no hydroxyl groups the spectrum consists essentially of a single intense band near 247 mμ. When hydroxylated solvents are used the 247 mμ band is weakened and a second band appears near 273 mμ. The energy difference between these bands is large, being 3850 cm.$^{-1}$ or 11.0 kcal/mole. The shift is much larger than the usual solvent effect, which is typically 5–10 mμ[4] compared to about 25 mμ here.

Figure 2 shows the spectrum of I obtained in a series of solvents made up of various proportions of acetonitrile and water. It is seen that as the solvent becomes richer in water, there is a steady weakening of the 247 mμ band and a steady intensification of the 275 mμ one but that there is virtually no shift in the band positions. This is quite unlike the case described by Brooker, Keyes and Heseltine[5] in which a single band shifted in wave length from the value for one pure solvent to that for the other. Furthermore the addition of a small trace of water to acetonitrile does not produce a dis-

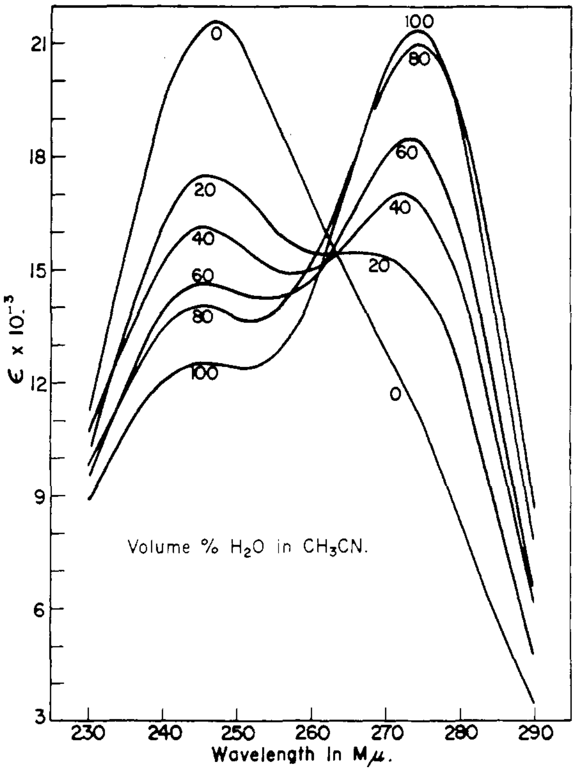


Fig. 2.—Spectrum of 1,8-bisdiazo-2,7-octanedione (I) in mixtures of water and acetonitrile. Numbers are the volume per cent of water; ε in liter/mole cm.

---

[3] It is difficult to write a satisfactory valence bond structure for the N_2CH— group. It is usually thought of as a resonance hybrid of $\overset{-}{N}=\overset{+}{N}=CH$— and $N\equiv\overset{+}{N}-\overset{-}{C}H$—, but for simplicity we shall usually write merely N_2CH—.

[4] A. E. Gillam and E. S. Stern, "Electronic Absorption Spectroscopy," Edw. Arnold Ltd., London, 1954, pp. 50, 263 ff.

[5] L. G. S. Brooker, G. H. Keyes and D. W. Heseltine, THIS JOURNAL, **73**, 5350 (1951).

Table I

Wave Lengths and Intensities of the Band Peaks

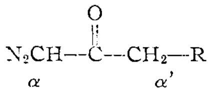
Compound	Solvent	λ_{max}, mμ	ϵ_{max}, l./mole cm.[a]
I	Dioxane	247 ...	24,800 ......
	Cyclohexane	247 ...	23,800 ......
	CH_3CN	247, ~275 w.sh.[f]	22,000 ......
	CH_2Cl_2	248, ~275 w.sh.	22,000 ......
	Chloroform	248, ~273 sh.	21,200 ......
	Ethanol	248, 270	19,100, ~16,700
	n-Propyl alcohol	247, ~269	18,100, ~15,700
	Ethylene glycol	248, 274	17,200, 18,100
	n-Butyl alcohol	245, ~270	16,000, ~13,700
	H_2O (*p*H 7.0)	245, 275	13,200, 22,500[b]
	Gl. acetic acid	...,[c] 273	 16,700
II	CH_2Cl_2	251, ...	6,840, ...
	EtOH	250, ~270	6,990, ...
	H_2O	~247, 275	4,600, 6600
III[d]	Cyclohexane	247, 290	1,360, 970
	CH_2Cl_2	249, 295	1,300, 1160
	EtOH	247, 302	1,230, 1300
	n-Butyl alcohol	~247, 304	1,060, 1420
IV	H_2O	241, 287	6,960, 11,100
V	CH_2Cl_2	247 ...	12,100 ......
	EtOH	247 ...	13,540 ......
	H_2O	249 ...	[e]

[a] $a = (1/bc) \log_{10}(I_0/I)$. [b] Fusari, *et al.* (ref. 1b), give 12,300 and 22,800 at *p*H 7.0. [c] Solvent absorption prevented measurement. [d] Insoluble in water. [e] Decomposition had occurred. Fusari, *et al.* (ref. 1b), give 18,240. [f] w.sh. = weak shoulder.

proportionately large effect, as is observed with some solvent pairs.[6] Rather there is a smooth transition from the spectrum in pure acetonitrile to that in pure water. Finally, the same results are obtained regardless of whether one starts with a solution in acetonitrile and adds water or with a solution in water and adds acetonitrile.

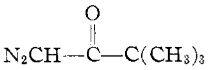
It will be noted that the curves of Fig. 2 pass approximately through a common point. It is well known that when a family of spectral curves taken under different conditions exhibits an isosbestic point, this constitutes proof of an equilibrium between two molecular species.[7] One can scarcely expect a true isosbestic point under the conditions of Fig. 2 because the solvent is changing from acetonitrile to water, and the usual solvent shifts due to change in refractive index are superimposed on the shift in equilibrium. In view of this we believe that Fig. 2 constitutes proof for an equilibrium between two forms of I.

One of the most obvious possibilities for an equilibrium is a keto–enol tautomerism. It is therefore of interest to know whether the solvent-induced spectral shift requires the presence of α- and/or α′-hydrogen atoms in the system



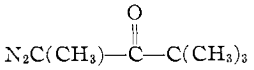
$$\mathrm{N_2\underset{\alpha}{CH}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\underset{\alpha'}{CH_2}{-}R}$$

This was tested by examining the spectra of 1-diazo-3,3-dimethyl-2-butanone (II), 1-diazo-1,3,3-trimethyl-2-butanone (III) and 6-diazo-5-keto-2-aminoheptanoic acid (IV) (see Fig. 3).



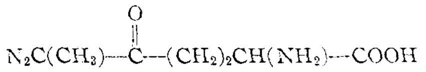
$$\mathrm{N_2CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}C(CH_3)_3}$$

II



$$\mathrm{N_2C(CH_3){-}\overset{\overset{\displaystyle O}{\|}}{C}{-}C(CH_3)_3}$$

III

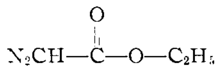


$$\mathrm{N_2C(CH_3){-}\overset{\overset{\displaystyle O}{\|}}{C}{-}(CH_2)_2CH(NH_2){-}COOH}$$

IV

The spectrum of II in methylene chloride has only the usual band near 250 mμ, whereas in ethanol there are two at 250 and 270 mμ. It therefore behaves like I. With III, in which all the potentially active hydrogens have been replaced, there was difficulty because of decomposition (see Experimental section). There was a strong second band at 290–304 mμ in the four solvents used, but in each case its intensity increased with time. We believe it is entirely due to decomposition products, although we never succeeded in obtaining a spectrum which did not have it. In other words, we believe but have not proved that pure III has only a 250 mμ band in any solvent. Compound IV has two bands, at 241 and 287 mμ, in aqueous solution. Unfortunately it was not examined in other solvents (being available to us only before this study was undertaken), so we cannot be certain that these are the analogs of the 248 and 275 mμ bands observed for I. However, it is probable that they are, for the amino acid group contributes virtually no absorption above 230 mμ. It appears, then, that the spectral shift with solvent requires either an α- or an α′-hydrogen, although the evidence from III is not as definite as one would like.

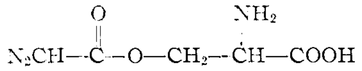
On the other hand, not all molecules having such available hydrogens show the effect. The spectrum of ethyl diazoacetate (V) was obtained in



$$\mathrm{N_2CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}C_2H_5}$$

V

water, ethanol and methylene chloride, and in each case there was only one band near 248 mμ (see Fig. 3). This corroborates some earlier results of Wolf,[8] who found that its band peak changed only 1–2 mμ when a number of solvents were compared. Azaserine (VI) also has only one band in aqueous



$$\mathrm{N_2CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}CH_2{-}\overset{\overset{\displaystyle NH_2}{|}}{C}H{-}COOH}$$

VI

solution at *p*H 7.0, at 250.5 mμ.[1a] These last two examples suggest that diazoacetyl esters in general do not show the effect.

Discussion and Further Results

Several possible causes for this spectral shift have been considered. The effect is not simply proportional to the dielectric constant of the solvent. However, the solvents do seem to fit into the sequence of their proton-donating ability. In solvents with relatively active hydrogens, such as water and acetic acid, the 275 mμ band is dominant. In solvents with less active hydrogens, such as ethanol, propanol, *n*-butyl alcohol and ethylene glycol, the two bands are of about equal intensity. In solvents with only a very slightly active hydro-

---

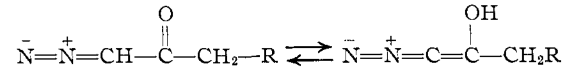
(6) W. R. Brode, "Chemical Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1939, pp. 183–184.

(7) W. West, in "Technique of Organic Chemistry," A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1949, Vol. I, Part II, p. 1299.

(8) E. Wolf, *Z. physik. Chem.*, **B17**, 46 (1932).

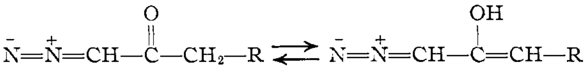
gen, such as chloroform, methylene chloride and acetonitrile, the 247 mμ is dominant, but a slight shoulder can be seen near 270 mμ. Finally in cyclohexane and dioxane, with no active hydrogens, there is no sign of even a shoulder; only the 247 mμ band is evident (see Fig. 1.)

At first a keto-enol tautomerism appeared to be the most likely explanation. This would be of the form



$$\overset{-}{N}=\overset{+}{N}=CH-\overset{O}{\overset{\|}{C}}-CH_2-R \rightleftarrows \overset{-}{N}=\overset{+}{N}=C=\overset{OH}{\overset{|}{C}}-CH_2R$$

or



$$\overset{-}{N}=\overset{+}{N}=CH-\overset{O}{\overset{\|}{C}}-CH_2-R \rightleftarrows \overset{-}{N}=\overset{+}{N}=CH-\overset{OH}{\overset{|}{C}}=CH-R$$

It is not possible to use the classical bromine addition test for an enol form, for this rapidly decomposes diazo ketones. When infrared spectra of diazo ketones are obtained in methylene chloride or chloroform solutions, there is no evidence for the characteristic OH band at 3200–3400 cm.$^{-1}$. We conclude that in these solvents the diazo ketone must be in the keto form and that the enol form occurs in those solvents where the 275 mμ band is well developed. In other words, the 247 mμ band is characteristic of the keto form, the 275 mμ band is characteristic of the enol form. Unfortunately all of the solvents in which the presumed enol form is present at appreciable concentration are themselves hydroxyl compounds, and there is no hope of finding the enol hydroxyl in the great excess of solvent hydroxyl by infrared spectroscopy.

As an alternative to this we have measured the infrared intensity of the carbonyl band of I in methylene chloride and in *n*-butyl alcohol. By comparing the ultraviolet spectrum of I in these two solvents, it appears that in going from methylene chloride to *n*-butyl alcohol the equilibrium shifts to give about 27% of the postulated enol form. If this is so, the carbonyl band intensity should be 27% lower in *n*-butyl alcohol than in methylene chloride. Actually, although the frequency shifts from 1640 cm.$^{-1}$ in methylene chloride to 1625 cm.$^{-1}$ in *n*-butyl alcohol and the band shape changes, the integrated intensities are almost identical (96 and 99, respectively, in arbitrary units). This indicates no decrease in the concentration of the carbonyl group and discredits the keto-enol postulate.[9]

Unfortunately this argument is not as conclusive as one would like. It is well known that the integrated intensity of an infrared carbonyl band depends on the solvent,[10] and it can be argued that in *n*-butyl alcohol the intensity has been enhanced by enough to compensate for the lower concentration.

We have also looked for new infrared bands appearing in the *n*-butyl alcohol solution which might be attributed to one or another of the triene structures, but without success.

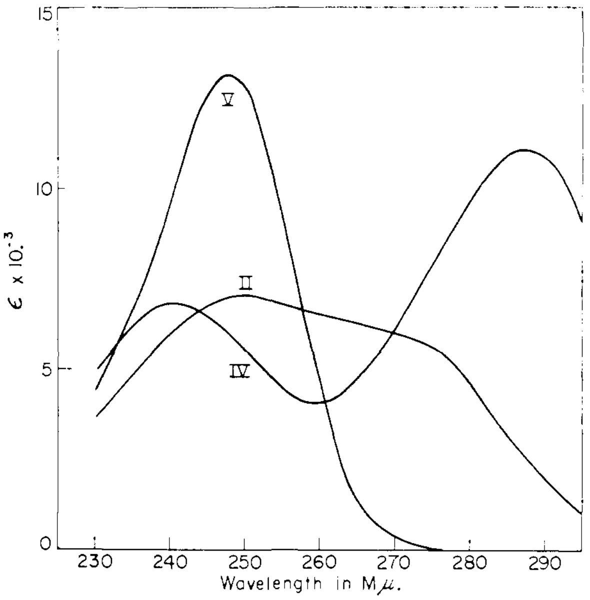
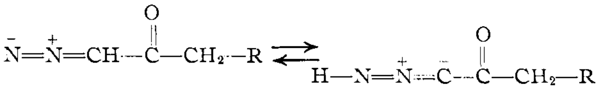


Fig. 3.—Spectra of other diazo compounds (ε in liter/mole cm.): II, $N_2CHCOC(CH_3)_3$ in ethanol; IV, $N_2\underset{CH_3}{\underset{|}{C}}-\underset{O}{\underset{\|}{C}}-CH_2CH_2\underset{NH_2}{\underset{|}{C}H}COOH$ in water; V, $N_2CHCOOC_2H_5$ in ethanol.

Finally, the intensity of the infrared diazo band at 2094 cm.$^{-1}$ was measured, this time in *n*-propyl alcohol and methylene chloride. The band contours are similar in the two solvents, the frequencies are the same and the integrated intensity in *n*-propyl alcohol is 21% less than in methylene chloride. In the ultraviolet, the intensity of the 247 mμ band in *n*-propyl alcohol is 20% less than in methylene chloride.

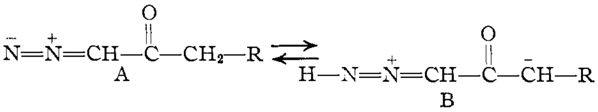
Thus we find on changing solvents that the infrared intensity of the diazo group diminishes by the same ratio as the intensity of the 247 mμ ultraviolet band (about 20%) but that the infrared intensity of the carbonyl group remains the same. If the change in intensities could only be assumed equal to the change in concentrations, this evidence would eliminate a keto-enol tautomerism. Unfortunately one cannot make this assumption, because of the varying effect of solvents on the intensity of a given infrared band. Consequently the evidence does not allow us to eliminate a keto-enol tautomerism, but it has encouraged us to look for another kind of equilibrium.

An alternative explanation, which seems to us to be more satisfactory, is to postulate a tautomerism of the diazo-isodiazo type



$$\overset{-}{N}=\overset{+}{N}=CH-\overset{O}{\overset{\|}{C}}-CH_2-R \rightleftarrows H-N=\overset{+}{N}=\overset{-}{C}-\overset{O}{\overset{\|}{C}}-CH_2-R$$

or possibly



$$\underset{A}{\overset{-}{N}=\overset{+}{N}=CH-\overset{O}{\overset{\|}{C}}-CH_2-R} \rightleftarrows \underset{B}{H-N=\overset{+}{N}=CH-\overset{O}{\overset{\|}{C}}-\overset{-}{C}H-R}$$

Form B would be characterized by an N–H band. Since none is observed in the infrared spectrum of a methylene chloride solution of I, presumably such

---

[9] We have found the carbonyl frequency of a number of diazo ketones to be near 1640 cm.$^{-1}$, which is abnormally low for a carbonyl frequency. The further lowering to 1625 cm.$^{-1}$ in butanol solution in the example above is probably the result of hydrogen bonding between the solvent and the carbonyl group.

[10] N. S. Bayliss, A. R. H. Cole and L. H. Little, *Aust. J. Chem.*, **8**, 26 (1955).

a solution contains primarily form A. Form B then is relatively more prevalent in hydroxylated solvents, where it would be impossible to find the N–H infrared band. A, then, is characterized by the 247 mμ band, B by the 275 one.

With this equilibrium, the diazo group should become less concentrated in going from A to B, whereas the carbonyl concentration should remain constant. This is exactly the way the corresponding infrared intensities behave. This equilibrium must therefore be considered as an alternative to the keto–enol tautomerism.

There is some precedent in the literature for postulating such a tautomerism, at least if diazomethane is a valid analog. Müller and Ludsteck[11] have shown that, with care, an iso form of diazomethane can be prepared, whose structure they propose as $\mathrm{H{-}\bar{C}{=}\overset{+}{N}{-}N{-}H} \longleftrightarrow \mathrm{H{-}C{\equiv}\overset{+}{N}{-}\bar{N}{-}H}$. Mills and Thompson,[12] when measuring the rotational fine structure of some infrared bands of gaseous diazomethane, observed a curious doubling of many of the lines which they attributed to the iso form. It is possible that a similar tautomerism may occur in substituted diazomethanes of the type $N_2CH{-}CO{-}CH_2{-}R$.

We use the following model to "explain" why the iso form occurs only in hydroxyl-containing solvents. In going from the diazo to the iso form (A → B), an active proton from the solvent attaches itself to the terminal nitrogen atom. The charges then rearrange, making it possible for the α- or α'- hydrogen to leave the molecule and produce the iso diazo form. The hydroxyl group, being also a proton acceptor, can participate in this step also. Thus the requirement fundamentally is not that the solvent contain hydroxyl groups but that it be a good proton donor. Unfortunately this cannot be tested directly with mineral acids because they rapidly decompose diazo ketones.

In summary, a keto–enol tautomerism cannot be rigorously eliminated, but a diazo–isodiazo tautomerism fits the observations somewhat better.

Experimental

Spectroscopic Procedures.—All ultraviolet spectra were obtained with a Cary model 11 recording spectrophotometer; 1-cm. quartz cells were used, with dilutions as needed. All solvents were of commercial grade, checked for ultraviolet transparency before use. The dioxane was distilled from sodium under a stream of dry nitrogen to remove peroxides, and the acetonitrile and *n*-propyl alcohol were distilled to remove absorbing impurities. All three were transparent to below 220 mμ after treatment.

The integrated infrared band intensities were measured on a Perkin–Elmer model 112 spectrometer (single beam, double pass), using prisms of NaCl or CaF_2. The optical path was flushed with dry air when working in the region of water absorption. Band areas were measured with no corrections for wings nor for finite slit widths.

Origin of the Compounds.—1,8-Bisdiazo-2,7-octanedione (I) was prepared by Dr. M. S. Morgan by a method previously described.[2] The clear yellow crystals melted at 71–73°.

1-Diazo-3,3-dimethyl-2-butanone (II) was prepared by Dr. H. A. DeWald by adding trimethylacetyl chloride (prepared from trimethylacetic acid and PCl_3) to an ether solution of diazomethane in the cold according to the Arndt–Eistert[13] synthesis. It was obtained as a dark red liquid which decomposed rather readily.

1-Diazo-1,3,3-trimethyl-2-butanone (III) was prepared by the Arndt–Eistert synthesis[13] by adding trimethylacetyl chloride to diazoethane in ether solution. Diazoethane was obtained by converting N-ethyl ethyl carbamate to N-ethyl-N-nitrosourethan and subjecting this to alkaline hydrolysis. III was a clear yellow liquid which slowly decomposed at room temperature. The presence of the diazo group was shown by the presence of a strong band at 2100 cm.$^{-1}$ in the infrared spectrum. In the ultraviolet spectrum, strong bands appeared at 249 and at 295 mμ in CH_2Cl_2 solution. On standing overnight, the 249 mμ band was weakened considerably with respect to that at 295 mμ. In the infrared the characteristic diazo band also weakened. It was concluded that the 295 mμ band is due at least partly, and perhaps entirely, to an impurity. It was also found upon examining this compound in different solvents that the position of the 249 mμ peak remained constant while the peak of the higher wave length band changed, being 290 mμ in cyclohexane, 295 in CH_2Cl_2, 302 in ethanol and 304 in *n*-butyl alcohol.

6-Diazo-5-keto-2-aminoheptanoic acid (IV) was prepared by Dr. H. A. DeWald and routinely examined before this study was initiated.

Ethyl diazoacetate (V) was a commercial sample. It was a clear yellow liquid which soon began to decompose when the sealed ampoule was opened.

Acknowledgment.—The authors are grateful to Drs. M. S. Morgan and H. A. DeWald of the Multiple Fellowship on Medicinal Chemistry for supplying most of the compounds used in this study and for many helpful discussions.

PITTSBURGH, PENNA.

---

[11] E. Müller and D. Ludsteck, *Chem. Ber.*, **87**, 1887 (1954).

[12] I. M. Mills and H. W. Thompson, *Trans. Faraday Soc.*, **50**, 1270 (1954).

[13] W. E. Bachmann and W. S. Struve, in "Organic Reactions," R. Adams, Ed., John Wiley and Sons, Inc., New York, N. Y., 1942, Vol. I, pp. 38 ff.