hexamethonium, as they have six carbons between nitrogens, and they differ from I only in having the three carbon side chain in the 4-position of the piperidine ring.

The products of type II are exact position analogs of I, but having only a three-carbon side chain and thus only five carbons between nitrogens they are also analogs of pentamethonium and of pentapyrrolidinium.

Both the bis-tertiary amines and the derived bis-quaternaries II of the 3-(3′-aminopropyl)-piperidine series were considerably more potent ganglionic blockers with a longer duration of action than the corresponding members of the 4 series III. Here, too, the most potent compounds were all bis-quaternary salts and several of these were equal to or better than hexamethonium. The bis-methiodides and bis-ethiodides of the 3-(3′-aminopropyl) (no. 2 and 3, Table IA) and of the 3-(3′-pyrrolidinopropyl) (no. 7 and 8, Table IA) piperidines were the best compounds of this series and showed potencies up to four times that of hexamethonium in the cat tests.

The pharmacology of these compounds will be reported elsewhere.

Acknowledgment.—The author is indebted to Mr. Samuel W. Blackman for the microanalyses and to Dr. Kenneth Colville for the pharmacological data.

Experimental

1-Methyl-3- and 4-(3′-chloropropyl)-piperidine Hydrochlorides.—The 3- and 4-(3′-hydroxypropyl)-pyridines were available commercially.[5] These were transformed into the 1-methyl-3(or 4)-(3′-chloropropyl)-piperidine hydrochlorides using the sequence of reactions outlined above. The methods were modifications of earlier procedures used successfully for related compounds.[6-8]

1-Methyl-3-(3′-chloropropyl)-piperidine hydrochloride melted at 119–120° after recrystallization from ethanol-ether mixtures.

Anal. Calcd. for $C_9H_{19}NCl_2$: C, 50.9; H, 9.0. Found: C, 50.8; H, 9.0.

1-Methyl-4-(3′-chloropropyl)-piperidine hydrochloride melted at 131–132° after recrystallization from ethanol-ether mixtures.

Anal. Calcd. for $C_9H_{19}NCl_2$: C, 50.9; H, 9.0. Found: C, 50.9; H, 9.0.

1-Methyl-3-(3′-pyrrolidinopropyl)-piperidine.—A mixture of 8.5 g. (0.04 mole) of 1-methyl-3-(3′-chloropropyl)-piperidine hydrochloride and 25 cc. of pyrrolidine was heated for 16 hr. at 100°. After removing excess pyrrolidine *in vacuo*, the product base was liberated with 25% aqueous alkali and was taken up in ether. The ether solution was dried over anhydrous potassium carbonate, the ether was evaporated and the residual oil was distilled *in vacuo*. The yield of pure base was 8 g. (95%) boiling at 153–154° at 17 mm.; dihydrochloride salt: m.p. 232–233° from alcohol–ether.

Dimethiodide.—A solution of 2.1 g. (0.01 mole) of the above base, 25 cc. of methanol and 5 cc. of methyl iodide was refluxed for 20 hr. After several recrystallizations from methanol–ethyl acetate mixtures the yield of white crystals was 4.9 g. (100%), m.p. 294–295° dec.

---

(5) These intermediates were purchased from the Reilly Tar and Chemical Co., Indianapolis, Indiana.

(6) A. W. Ruddy and H. W. Bishop, THIS JOURNAL, **74**, 1919 (1952).

(7) R. R. Burtner and J. M. Brown, *ibid.*, **69**, 630 (1947).

(8) T. R. Norton, R. A. Seibert, A. A. Benson and F. W. Bergstrom, *ibid.*, **68**, 1572 (1946).

TUCKAHOE 7, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

Aliphatic Diazo Compounds. III. Infrared Spectra[1,2]

BY PETER YATES AND BERNARD L. SHAPIRO[3] WITH NAOYA YODA AND JOSEPH FUGGER

RECEIVED MAY 6, 1957

The major bands in the region 2–12 μ of the infrared spectra of twenty-nine aliphatic diazo compounds are recorded and the relationship between their position and the structure of the diazo compounds is discussed.

Although two recent studies[4,5] of diazonium salts have codified the infrared spectra of many compounds of this type, no similar compilation appears to have been made for aliphatic diazo compounds, apart from the special case of diazoöxides.[5,6] It has been recognized for some time, however, that such compounds consistently show an intense absorption band in the 4.5–5 μ region, which has been used to confirm the presence of the aliphatic diazo group.[7] In the course of studies of the chemistry of aliphatic diazo compounds we have had occasion to examine their infrared spectra and it is the purpose of the present communication to report some tentative correlations on the basis of these observations.

Experimental

The diazo compounds were prepared by standard procedures to which references are given in Tables I and II. The spectra of solutions in carbon tetrachloride, dichloromethane or chloroform were recorded with a Perkin-Elmer Model 21 spectrophotometer using an NaCl prism. They were calibrated by the use of atmospheric carbon dioxide and water vapor, and a carbon monoxide gas cell.[8] Representative spectra are illustrated in Fig. 1.

Results

Diazohydrocarbons.—Table I records the bands in the 4.5–5 μ region for several diazohydrocarbons

---

(1) For previous papers in this series see P. Yates, THIS JOURNAL, **74**, 5376 (1952); A. K. Bose and P. Yates, *ibid.*, **74**, 4703 (1952).

(2) This work was supported in part by an institutional research grant from the American Cancer Society to Harvard University.

(3) Shell Foundation Fellow, 1955–1956.

(4) M. Aroney, R. J. W. Le Fèvre and R. L. Werner, *J. Chem. Soc.*, 276 (1955).

(5) K. B. Whetsel, G. F. Hawkins and F. E. Johnson, THIS JOURNAL, **78**, 3360 (1956).

(6) R. J. W. Le Fèvre, J. B. Sousa and R. L. Werner, *J. Chem. Soc.*, 4686 (1954).

(7) *Cf.*, for example, S. A. Fusari, T. H. Haskell, R. P. Frohardt and Q. R. Bartz, THIS JOURNAL, **76**, 2881 (1954).

(8) The band of carbon monoxide at 4.66 μ[9] was used for the calibration of the 4.5–5 μ region. Since previously published reports of bands in this region in the spectra of individual aliphatic diazo compounds have frequently failed to refer to calibration against a *close-lying* standard band, we have in general not included these bands with the present results.

(9) G. Herzberg, "Molecular Spectra and Molecular Structure. I.

TABLE I

SPECTRA OF DIAZOHYDROCARBONS AND DERIVATIVES (CCl_4 SOLUTION)

Compound	Wave length (μ)	Ref.
CH_2N_2	4.82	*a*
p-NO_2-$C_6H_4CHN_2$	4.88	*b*
CH_3CHN_2	4.91	*a*
$C_2H_5CHN_2$	4.89	*c*
$C_3H_7CHN_2$	4.90	*a*
$C_6H_5CHN_2$	4.91	*d*
(*p*-NO_2-$C_6H_4)_2CN_2$	4.92	*e*
$(C_6H_5)_2CN_2$	4.94	*f*
$C_6H_5CH_2CN_2C_6H_5$	4.95	*f*
(*p*-Me_2N-$C_6H_4)_2CN_2$	4.97[g]	*f*

[a] Prepared in the usual manner from the corresponding N-alkyl-N-nitrosourea; *cf.* W. E. Bachmann and W. S. Struve, "Organic Reactions," Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 50. [b] T. Curtius and A. Lublin, *Ber.*, **33**, 2460 (1900). [c] D. W. Adamson and J. Kenner, *J. Chem. Soc.*, 1551 (1937). [d] From the alkaline cleavage of phenylbenzoyldiazomethane (P. Yates and B. L. Shapiro, unpublished results). [e] Kindly supplied by Professor F. Greene, Massachusetts Institute of Technology. [f] Prepared by the mercuric oxide oxidation of the corresponding hydrazone; *cf.* L. I. Smith and K. L. Howard, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 351. [g] Chloroform solution.

TABLE II

SPECTRA OF DIAZOCARBONYL COMPOUNDS (CH_2Cl_2 SOLUTION)

Compound		Wave lengths (μ)			Ref.
$RCOCHN_2$ R					
C_6H_5		4.78	6.17	7.36	*a*
p-MeO-C_6H_4		4.76	6.17	7.37	*a,b*
3,4,5-$(MeO)_3C_6H_2$		4.76	6.16	7.40	*a,c*
p-NO_2-C_6H_4		4.76	6.14	7.44	*a*
α-$C_{10}H_7$		4.79	6.14, 6.20	7.42, 7.49	*a*
β-$C_{10}H_7$		4.78	6.20[d]	7.32, 7.47	*a*
Me		4.78	6.07	7.32, 7.49	*a*
3,4,5-$(MeO)_3C_6H_2CH_2CH_2$		4.78	6.08	7.33	*a,c*
$CH_3(CH_2)_{16}$		4.79	6.09	7.37	*a,e*
$CH_3(CH_2)_{17}$		4.79	6.09	7.36	*a,e*
$RCOCR'N_2$ R	R′				
C_6H_5	C_6H_5	4.85	6.16[d]	7.41	*f*
p-Cl-C_6H_4	*p*-Cl-C_6H_4	4.85	6.14[d]	7.47	*f*
C_6H_5	Et	4.85	6.20[d]	7.42	*a*
p-Cl-C_6H_4	Me	4.86	6.23[d]	7.46	*a*
β-$C_{10}H_7$	Me	4.86	6.22[d]	7.38, 7.51	*a*
α-Diazocamphor		4.86	5.94	7.33	*f,g*
α-Diazoacenaphthenone		4.82	5.95	7.23	*f*
$N_2CHCOOEt$		4.76	5.90	7.27, 7.42	*h*
$C_6H_5CH(OAc)COCN_2COOEt$ (IX)		4.69	5.75, 5.83, 5.99	7.28	*b*

[a] Prepared in the usual manner from the corresponding acid chloride and diazohydrocarbon in ether solution; *cf.*, F. Arndt and J. Amende, *Ber.*, **61**, 1122 (1928). [b] Kindly supplied by Dr. A. S. Kende. [c] Kindly supplied by Dr. J. B. Hendrickson. [d] Composite band. [e] F. A. Vandenheuvel and P. Yates, *Can. J. Res.*, **B28**, 556 (1950). [f] Prepared by the mercuric oxide oxidation of the corresponding monohydrazone; *cf.*, C. D. Nenitzescu and E. Solomonica, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 496. [g] Kindly supplied by Dr. J. Huffman. [h] K and K Laboratories, Long Island City, New York.

and closely related derivatives.[10] These were all recorded in carbon tetrachloride solutions, with one exception; in the case of diphenyldiazomethane it was found that the band fell in the same position when solutions in carbon tetrachloride, dichloromethane and carbon disulfide were examined. In every case this band was of strong intensity and was the only intense band observed in the 2–12 μ range, apart from the bands which readily could be attributed to structural features other than the diazo group. A consistent shift to longer wave lengths may be noted as either alkyl or aryl groups are substituted for the hydrogen atoms of diazomethane; thus, while the band of diazomethane falls at 4.82 μ, those of the monosubstituted diazomethanes occur in the range 4.88–4.91 μ, while the disubstituted derivatives absorb in the range 4.92–4.97 μ. Further, it may be observed that *p*-substitution by nitro groups on the phenyl substituted diazomethanes leads to a small shift of the band to lower wave lengths, while *p*-substitution by the dimethylamino group brings about a shift in the opposite sense.

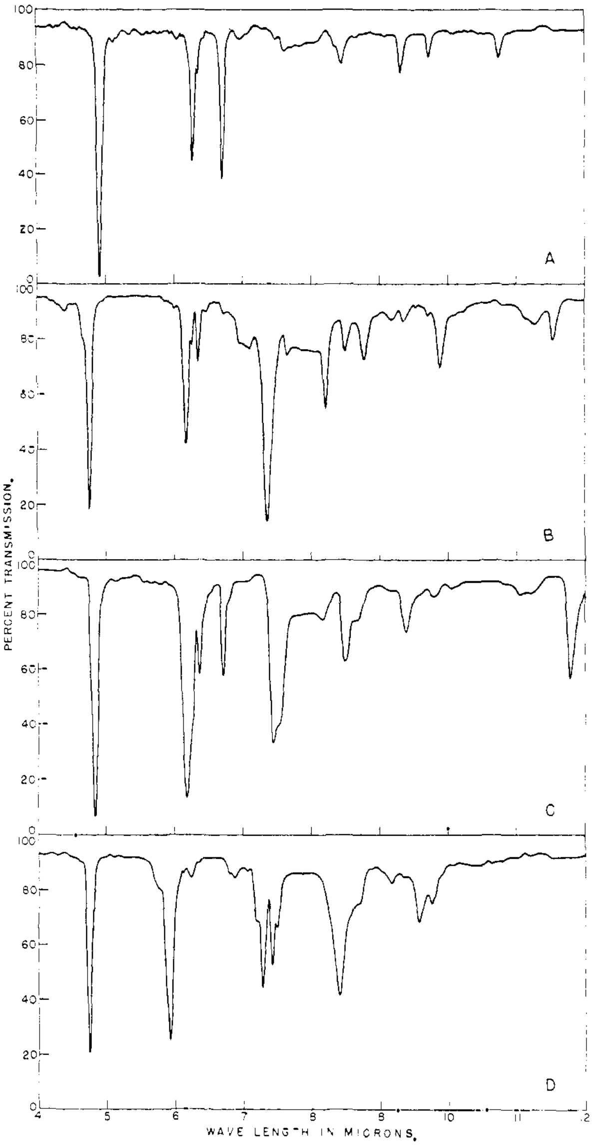


Fig. 1.—Infrared spectra in CH_2Cl_2 solution: A, diphenyldiazomethane; B, α-diazoacetophenone; C, azibenzil; D, ethyl diazoacetate.

Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., 2nd ed., New York, N. Y., 1950, pp. 53–54.

[10] In most instances this intense band is accompanied by one or more adjoining weak bands or shoulders in the range 4.4–4.65 μ.

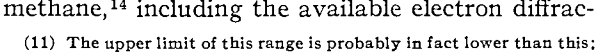
Diazoketones.—In Table II are recorded the three major bands which are present in the spectra of all of the diazoketones examined (in solution in dichloromethane). Each of them shows an intense band in the same general region as the intense bands of the diazohydrocarbons; in the case of the diazoketones of type $RCOCHN_2$ this falls in the narrow range 4.76–4.79 μ, while in the case of those of type $RCOCR'N_2$ it falls in the narrow, but higher, range 4.82–4.86 μ (it may be noted that six of the seven compounds examined show this band at 4.85–4.86 μ). The second intense band occurs in the region 6.07–6.23 μ[11] for both types of diazoketone, with the exception of diazocamphor and diazoacenaphthenone which have strong bands at 5.94–5.95 μ. Further, apart from these two compounds, in the cases where R is aliphatic this band falls in the region 6.07–6.08 μ, while when R is aromatic the range is appreciably higher, *viz.*, 6.14–6.23 μ.[11] Finally, all of the diazoketones have a very intense band (frequently the strongest band in the 2–12 μ region) in the region 7.2–7.5 μ; in some of the compounds a composite band or two strong bands occur in this region. Several diazoketones showed medium or strong bands beyond 7.5 μ; however, no consistent band pattern could be discerned in this region and several of these bands could be attributed to structural features other than the diazoketone grouping.

Diazoesters.—Table II also includes the spectra of two diazoesters. They show bands similar to those of the diazoketones, although the position of the bands is changed to some extent.

Discussion

The sole aliphatic diazo compound whose spectrum has been subjected to detailed analysis is diazomethane. Crawford, Fletcher and Ramsay[12] have made vibrational assignments on the basis of a study of the spectra of diazomethane and deuterated diazomethane; the diazomethane spectrum also has been studied by Mills and Thompson.[13] These investigators are in agreement in assigning the intense parallel type band observed at 4.76 μ for gaseous diazomethane to the stretching vibration of the N–N bond. The intense band at 4.82 μ which we have observed for diazomethane in solution must undoubtedly also correspond to this vibration.

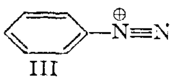
In terms of resonance theory, diazomethane is best represented as a hybrid to which two structures, I and II, make major, and comparable, contributions.



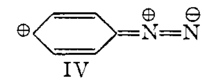
$$\overset{\ominus}{C}H_2-\overset{\oplus}{N}\equiv N \longleftrightarrow CH_2=\overset{\oplus}{N}=\overset{\ominus}{N} \longleftrightarrow \text{other less important structures}$$

I II

This view is in accord with the properties of diazomethane,[14] including the available electron diffraction data[15,16] and dipole moment measurements on substituted diazomethanes.[17] The appearance of the N–N stretching band of diazomethane at a longer wave length than that of benzenediazonium salts (*e.g.*, 4.40 μ for the borofluoride)[5] may be interpreted on this basis. It is to be anticipated that structures such as IV make a considerably smaller contribution to the benzenediazonium cation hybrid than does II to the diazomethane hybrid since they are relatively of higher energy due to the separation of charge.[18] Thus the N–N bond in diazomethane would be expected to have less triple bond character than that in the diazonium ion, resulting in a shift of the N–N band to higher wave lengths.



III



IV

The consistent shift of this band to yet longer wave lengths in the case of substituted diazohydrocarbons is unusual in that it is observed to be largely dependent on the number, rather than the nature, of the substituents. This shift may be due in part to a simple mass effect, which is observed in the case of carbonyl compounds.[19] However, that this cannot be the most important factor is demonstrated by the very small shift brought about by the deuteration of diazomethane.[12,20] The major cause of this shift is obscure, but it may be suggested that it is in part dependent on the fact that this band does not arise from an isolated N–N vibration, but one which is coupled to a considerable degree with vibration of the C–N bond; substitution on the carbon atom might well affect this coupling and thus the position of the band.[21] The similarity in position of this band in both alkyl and aryl substituted diazohydrocarbons of the same degree of substitution is in marked contrast to the well known shifts brought about in the C–O stretching frequencies of carbonyl compounds on replacement of alkyl by aryl substituents.[22,23] The additional contributors to the resonance hybrids of aryldiazohydrocarbons may be of two types, exemplified by V and VI, in contradistinction to the case of carbonyl compounds where only contributors of type VII, with negative charge on oxygen

---

(11) The upper limit of this range is probably in fact lower than this; certain of the bands included are composite, due to overlap with aromatic bands.

(12) B. L. Crawford, W. H. Fletcher and D. A. Ramsay, *J. Chem. Phys.*, **19**, 406 (1951); *cf.*, also, D. A. Ramsay, *ibid.*, **17**, 666 (1949); W. H. Fletcher and T. P. Garrett, *ibid.*, **25**, 50 (1956).

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

(14) R. Huisgen, *Angew. Chem.*, **67**, 439 (1955); P. Yates, Ph.D. Thesis, Yale, 1951.

(15) H. Boersch, *Monatsh.*, **65**, 331 (1935).

(16) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 181.

(17) N. V. Sidgwick, L. E. Sutton and W. Thomas, *J. Chem. Soc.*, 406 (1933).

(18) Indeed, Whetsel, Hawkins and Johnson[5] have concluded that since the spectra of benzenediazonium salts, other than those bearing a *p*-amino group, show a band between 4.36 and 4.47 μ, close to the position of the Raman band of nitrogen, there is little resonance of any kind between the aromatic ring and the $-N_2^{\oplus}$ group, and the structure of the benzenediazonium cation is best represented by III.

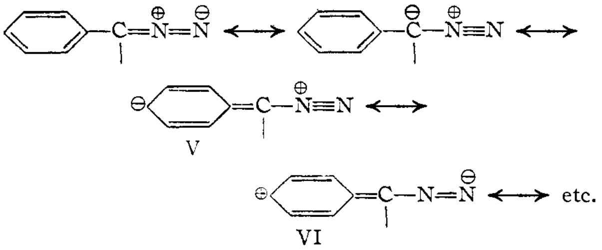
(19) R. N. Jones and C. Sandorfy in "Chemical Applications of Spectroscopy," W. West, ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 473.

(20) The shift of 0.01 μ may be compared with that of 0.14 μ reported to result on deuteration of formaldehyde.[19]

(21) Thus, the relative amounts of stretchings of the N–N and C–N bonds in this vibration mode of diazomethane are 0.372 and 0.232, respectively. These figures were made available to us by Professor B. L. Crawford, University of Minnesota, whom we cordially thank for this and additional information on the spectrum of diazomethane.

(22) Reference 19, p. 448.

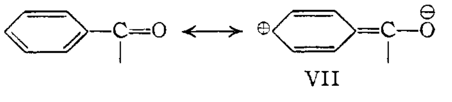
(23) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen & Co., London, 1956, p. 119.



V

VI

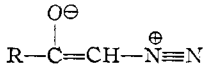
and analogous to type VI, are important. The lack of shift on the substitution of phenyl for alkyl in the diazohydrocarbons is attributable to the op-



VII

posing effects on the stretching of the N–N bond engendered by the two types of contributor, V and VI.[24] This concept is in harmony with the small observed shifts brought about by the substitution of nitro and dimethylamino groups in the *para* position of the phenyl rings of diazohydrocarbons. In the former case a shift to shorter wave lengths results, consonant with the anticipated increased importance of contributors of type V, relative to type VI, due to the distribution of the negative charge on to the nitro group, leading to increased triple bond character of the N–N bond. In the latter case, the dimethylamino groups may be expected to increase the importance of contributors of type VI, relative to type V, leading to a shift in the opposite sense.[25] It is of relevance to note that similar relationships are apparent from data reported for the asymmetric N–N–N vibration of the azides[26]; the position of this band is little changed by substitution of phenyl for alkyl groups, but falls to lower wave lengths when the phenyl ring bears *o*- or *p*-nitro-substituents.

The position of the similar band in the diazoketones can be interpreted readily in similar terms if comparison is made with diazohydrocarbons *of the same degree of substitution.* Thus the diazoketones of type RCOCHN$_2$ have this band shifted to lower wave lengths, relative to diazohydrocarbons of type RCHN$_2$, by *ca.* 0.12 μ, while those of type RCOCR'N$_2$ show a similar shift of *ca.* 0.09 μ, relative to diazohydrocarbons of type RR'CN$_2$. These shifts may be attributed to the major importance of contributors of type VIII, bearing the



$$R-\overset{O^{\ominus}}{\overset{|}{C}}=CH-\overset{\oplus}{N}\equiv N$$

VIII

negative charge on the carbonyl oxygen, in the resonance hybrid of diazoketones,[14] leading to a considerable increase in the triple bond character of the N–N bond. Similar effects are apparent in the spectra of ethyl diazoacetate and ethyl 1-acetoxy-2-diazo-3-oxo-1-phenylbutyrate (IX); in the latter case the position of the band, 4.69 μ, is appreciably lower than that for any other diazocarbonyl compound examined, clearly compatible with the fact that conjugation with two carbonyl groups will still further increase the triple bond character of the N–N bond. Again an analogy with the azides is apparent in that a shift of 0.12 μ to lower wave lengths has been reported for methyl azidocarboxylate relative to alkyl azides.[27,28]

The intense bands in the 6 μ region of the diazoketone spectra may reasonably be assigned to the carbonyl stretching vibration. Their position is readily rationalized in the above terms. The considerable shift to longer wave lengths relative to the carbonyl stretching bands of simple ketones results from the strong resonance interaction exemplified by VIII. In general, in the case of the aliphatic diazoketones this brings about a shift of *ca.* 0.23 μ, relative to aliphatic ketones; a further shift of 0.07–0.16 μ[11] is observed for aromatic diazoketones, due to additional conjugation of the carbonyl group with the aromatic ring. The two diazoketones which have their carbonyl band below 6 μ, diazocamphor and diazoacenaphthenone, both contain the ketonic function in a five-membered ring, a circumstance which ha long been known to shift

TABLE III

	Region (μ)[a]	Reference
Aromatic diazonium salts	4.33–4.68	*b*
Isocyanates	4.40–4.46	*c*
Nitriles	4.42–4.51	*d*
Azides	4.63–4.75	*e*
Ketenes	(4.63, 4.70)[f]	*g*
Carbodi-imides	4.65–4.76[h]	*i*
Aliphatic diazo compounds	4.69–4.97[j]	
Allenes	5.0–5.26[h]	*k*

[a] In some cases the region reported must be considered as approximate, since not all of these spectra have been adequately calibrated, *cf.* reference 8. [b] *Cf.* refs. 4, 5. [c] H. Hoyer, *Ber.*, **89**, 2677 (1956); W. H. T. Davison, *J. Chem. Soc.*, 3712 (1953). [d] R. E. Kitson and N. E. Griffith, *Anal. Chem.*, **24**, 334 (1952). [e] *Cf.* ref. 26. [f] These are the positions for ketene and diphenylketene, respectively. [g] D. H. Whiffen and H. W. Thompson, *J. Chem. Soc.*, 1005 (1946); L. G. Drayton and H. W. Thompson, *ibid.*, 1416 (1948). [h] In certain cases two bands are reported in this region. [i] G. D. Meakins and R. J. Moss, *J. Chem. Soc.*, 993 (1957). [j] The range is 4.76–4.97 μ if the exceptional case of compound IX (see Table II) is excluded. [k] J. H. Wotiz and D. E. Mancuso, *J. Org. Chem.*, **22**, 207 (1957).

---

(24) It is realized that interpretations of the shifts of this band in terms of the N–N bond are at best approximate, due to the complex nature of the vibration.[21] However, the consistent pattern which emerges from such an interpretation encourages us to consider that such an approximation is justified; *cf.* earlier designations of this band in diazomethane as an N–N stretching vibration.[12,18]

(25) *Cf.* the similar type of shift in *p*-aminobenzenediazonium salts, which has been discussed in similar terms.[5]

(26) Yu. N. Sheinker and Ya. K. Syrkin, *Isvest. Akad. Nauk S.S.S.R. Ser. Fiz.*, **14**, 478 (1950).

(27) The positions reported for the corresponding bands of 1,4-benzenediazoöxide and 4-nitro-2,1-benzenediazoöxide (4.74, 4.58 and 4.65 μ, respectively, in Nujol mulls) are also in accord with these views.[5] Certain naphthalenic diazoöxides have been reported to absorb in Nujol mulls at the remarkably high wave length of 4.96 μ[6]; however, in the course of other work we have had occasion to examine the spectra of 1,2-naphthalendiazoöxide and 2,1-naphthalenediazooxide in chloroform solution and have observed intense bands at 4.77 and 4.73 μ, respectively (P. Yates and E. W. Robb, THIS JOURNAL, **79**, 5760 (1957).

(28) Attention may here be drawn to the position reported for the diazo band of diazocyclopentadiene, *i.e.*, 4.80 μ.[29] This is considerably lower than the bands of other diazohydrocarbons of the same degree of substitution and the shift readily may be attributed to electronic factors similar to those discussed in the case of the diazocarbonyl compounds.

(29) W. von E. Doering and C. H. DePuy, THIS JOURNAL, **75**, 5955 (1953).

the carbonyl stretching frequency of simple ketones to shorter wave lengths.[30] The carbonyl band of ethyl diazoacetate also exhibits a similar type of shift to that found in the case of the diazoketones. The bands of IX at 5.75, 5.83, 5.99 μ may be assigned to the carbonyl stretching of the acetoxy, carbethoxy and ketonic groups, respectively; the two higher bands are shifted to longer wave lengths than those associated with simple carbethoxy and ketonic groups, but the shift is smaller than in the case of the monocarbonyl diazo compounds, attributable to the cross conjugation of the diazo group with two carbonyl groups.

The very intense bands in the 7.2–7.5 μ region observed for all the diazoketones and diazoesters are useful for diagnostic purposes, but at present no firm basis exists for the proposal of a vibrational assignment. It may be significant that the azides also show an intense band in this region which has been assigned to the symmetrical stretching mode of the N–N–N group. However, in the case of diazohydrocarbons there are no strong bands in this region, and in the case of diazomethane, Crawford, Fletcher and Ramsay have assigned to the C–N stretching vibration a band at 11.7 μ.[12]

Finally, it may be noted that this and other recent investigations permit useful distinctions to be made between the positions of bands falling in the 4.4–5.3 μ region for several different types of compound (see Table III).

CAMBRIDGE, MASS.

---

(30) Reference 19, p. 485; reference 23, p. 128.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

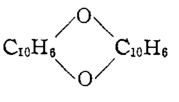
The Thermal Decomposition of Diazoöxides[1]

BY PETER YATES AND ERNEST W. ROBB[2]

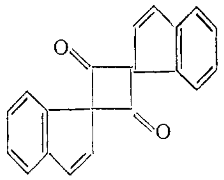
RECEIVED MAY 22, 1957

The product obtained by the decomposition of either naphthalene-1,2- or 2,1-diazoöxide in boiling xylene has been shown to be a 2-indenylidenenaphtho[1,2]-1,3-dioxole (XIII). It has been found to be accompanied by small amounts of its stereoisomer XIIIa. Thermal decomposition of naphthalene-2,1-diazoöxide in the presence of diphenylketene has been shown to give 2-benzohydrylidenenaphtho[1,2]-1,3-dioxole (XX). The mechanisms of these reactions are discussed.

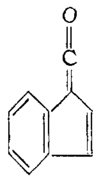
Although the course of the photolytic decomposition of diazoöxides has been elucidated in recent years as a result of the extensive work of Süs[3] and de Jonge[4] and their collaborators scant attention has been paid to the pyrolysis of this type of compound. Vaughan and Phillips[5] have observed that the gaseous products from the solid state pyrolysis of a number of diazoöxides consist mainly of nitrogen and carbon dioxide, while de Jonge[6] found that the same products are obtained when *o*-hydroxybenzenediazonium salts are heated in boiling water for some time. De Jonge proposed that the course of the thermal and photolytic decompositions are the same and that the carbon dioxide arises from decarboxylation of cyclopentadienecarboxylic acid derivatives, which have been shown to be formed in the course of the photolytic decomposition reactions.[3,4] However, neither he nor Vaughan[5] made any study of the non-gaseous products from the pyrolytic reactions. The only compounds which appear to have been examined in any detail are the naphthalene-1,2- and 2,1-diazoöxides. Bamberger[7] discovered that on heating either of these compounds in boiling xylene a product, $C_{20}H_{12}O_2$, m.p. 256°, was obtained which he formulated as a "bis-naphthalene-oxide" (I). Subsequently, Horner, Spietschka and Gross[8] investigated this product more thoroughly and came to the conclusion that the compound was the 1,3-cyclobutanedione derivative II formed by dimerization of the ketene III.



I



II



III

On the basis of the reported evidence the structure assigned seemed plausible; however, certain features of the degradative work appeared to us to require further clarification, *viz.* (i) the fact that the product obtained by hydrolysis of the pyrolysis product with aqueous acetic acid, which was assigned the formula $C_{20}H_{14}O_3$ and the structure IV, was not reported to undergo ready decarboxylation, although this would be anticipated on the basis of its formulation as both a β-keto acid and a cyclopentadienecarboxylic acid, (ii) the formation of a blue solution when this product was dissolved in aqueous sodium hydroxide, (iii) the observation that the compound obtained by hydrogenation of the hydrolysis product, which was assigned the formula $C_{20}H_{18}O_3$ and the structure V, gave a positive ferric chloride test, in spite of the fact that enolization of the ketone toward the carboxylic acid group of V is impossible. It was therefore de-

---

(1) From the Ph.D. Thesis of Ernest W. Robb, Harvard University, 1956; a preliminary account of part of this work has appeared previously: P. Yates and E. W. Robb, *Chemistry & Industry*, 794 (1956).

(2) Public Health Service Research Fellow of the National Heart Institute, 1955–1956.

(3) O. Süs, *Ann.*, **556**, 65, 85 (1944); **579**, 133 (1953); O. Süs, M. Glos, K. Möller and H. D. Eberhardt, *ibid.*, **583**, 150 (1953); O. Süs and K. Möller, *ibid.*, **593**, 91 (1955); O. Süs, K. Möller and H. Heiss, *ibid.*, **598**, 123 (1956); O. Süs and K. Möller, *ibid.*, **599**, 233 (1956).

(4) J. de Jonge and R. Dijkstra, *Rec. trav. chim.*, **67**, 328 (1948); J. de Jonge, and R. Dijkstra, *ibid.*, **68**, 426 (1949); J. de Jonge, R. J H. Alink and R. Dijkstra, *ibid.*, **69**, 1448 (1950).

(5) J. Vaughan and L. Phillips, *J. Chem. Soc.*, 1560 (1947).

(6) J. de Jonge, R. Dijkstra and P. B. Braun, *Rec. trav. chim.*, **68**, 430 (1949).

(7) E. Bamberger, M. Baum and L. Schlein, *J. prakt. Chem.*, **105**, 266 (1922).

(8) L. Horner, E. Spietschka and A. Gross, *Ann.*, **573**, 17 (1951).