silver nitrate test for chloride ion. The solid was then dried and extracted with petroleum ether (b.p. 60–90°) to give 5 g. of light brown, soluble material and 1.5 g. of dark brown, insoluble polymer.

Molybdenum Pentachloride and Mesitylene.—Molybdenum pentachloride (0.25 mole) was allowed to interact with mesitylene (1 mole) at 23–25° for 2.5 hr. Work-up gave 1.8 g. of colorless liquid, b.p. 65–67° (4 mm.), $n^{24}\text{D}$ 1.5250. The infrared spectrum was identical with that of an authentic sample of chloromesitylene.

Bimesityl, 20 g. (34% yield), was obtained as white crystals on continued vacuum distillation, b.p. 135–145° (3 mm.), m.p. 100.5–101.5° (from ethanol), the mixture melting point with authentic bimesityl was undepressed. A small amount of viscous, yellow oil, 0.5 g., b.p. 180–205° (3 mm.), was also collected. The residue comprised 1.9 g. of black, glassy solid.

Vanadium Tetrachloride and Benzene. 1.—Reaction of vanadium tetrachloride (0.42 mole) with benzene (1.6 moles) of 80° for 2.5 hr. gave chlorobenzene, b.p. 127–131°, 15.6 g. (66% yield), as the principal product. The infrared spectrum proved to be identical with that of authentic material. A small amount of dichlorobenzene, b.p. 170–176°, 0.5 g., having an isomer distribution predominantly *ortho–para*, was also obtained. Fractional distillation of the residue (about 0.1 ml.) through a short-path, semimicro apparatus, yielded a small quantity of white crystalline condensate (0.05 g.), m.p. 144–146°. The infrared spectrum was identical with that of 4,4′-dichlorobiphenyl. The ultraviolet spectrum and mixture melting point confirmed the identification.

2.—In the presence of water (0.1 mole), vanadium tetrachloride (0.2 mole) and benzene (0.8 mole) at 80° for 2.5 hr. gave 1.3 g. (12% yield) of chlorobenzene, b.p. 130–131°. Filtration of the reaction mixture, after addition of dilute acid, afforded 0.2 g. of yellow-brown solid whose infrared spectrum was very similar to that of *p*-polyphenyl (principal bands at 767, 807 (major), 1000, 1400, and 1483 cm.$^{-1}$).

Vanadium Tetrachloride and Mesitylene.—Vanadium tetrachloride (0.2 mole) and mesitylene (0.8 mole) at 25° for 2.5 hr. provided 3.2 g. (21% yield) of chloromesitylene, b.p. 51–56° (1.8 mm.), identified by comparison with authentic material. Bimesityl, 7.2 g. (30% yield), distilled at 136–165° (1.8 mm.), colorless crystals, m.p. 100–101° (from ethanol). Residual material weighed 0.8 g. (black solid).

Antimony Pentachloride and Benzene.—Reaction of antimony pentachloride (0.25 mole) and benzene (1 mole) at 80° for 2.5 hr. gave 20.9 g. (74% yield) of chlorobenzene, b.p. 130–131°, identified by comparison (infrared spectrum) with authentic material. A second fraction, 0.9 g., (4.9% yield), b.p. 170–176°, was identified (infrared analysis) as a mixture of dichlorobenzenes.

Isomerization of *o*-Bromochlorobenzene in the Presence of Molybdenum Pentachloride–Hydrogen Chloride.—A mixture of *o*-bromochlorobenzene (28.8 g., 0.15 mole) and molybdenum pentachloride (13.65 g., 0.05 mole) was heated at 108–110° for 2.5 hr. with good stirring while hydrogen chloride was passed into the mixture. The cooled reaction mixture was stirred with 18% hydrochloric acid and then extracted with methylene chloride. The organic portion, after being washed, was freed of solvent. The red-brown liquid residue, 28 g., was examined by gas chromatography (Aerograph 202, 40 cc./min. of helium, 185°, 5 ft. of SE-30 or FFAP on Chromosorb W). G.l.p.c. and infrared analyses indicated the presence of *o*- and *m*-bromochlorobenzene, but no *para* isomer. There were minor amounts of two higher molecular weight materials, presumably formed from chlorination or disproportionation.

Attempted Isomerization of *o*-Dichlorobenzene in the Presence of Molybdenum Pentachloride–Hydrogen Chloride.—A mixture of *o*-dichlorobenzene (45 g., 0.3 mole, g.l.p.c. pure) and molybdenum pentachloride (27.3 g., 0.1 mole) was heated with stirring at 110° for 2.5 hr. while hydrogen chloride was introduced below the surface. After treatment with 18% hydrochloric acid, the organic phase was washed with water and dried. Infrared and g.l.p.c. analyses of the recovered dichlorobenzene demonstrated the presence of only the *ortho* isomer. These analytical procedures revealed that 1,2,4-trichlorobenzene was formed in 12% yield.

Acknowledgment.—We gratefully acknowledge support provided by the National Science Foundation.

Structure and Reactivity of Methoxy-Substituted Benzenediazonium Cations

R. J. Cox and J. Kumamoto

IBM Research Laboratory, San Jose, California

Received August 13, 1965

A systematic relationship between the molecular structure of methoxy-substituted benzenediazonium salts and the N–N stretching frequency has been observed. This is useful in the identification and classification of these molecules. Resultant substituent constants, σ^+, for multiple substituted derivatives were assigned on the basis of their observed N–N frequencies and a Hammett ρ–σ correlation of the rate constants for the coupling reaction with 6-naphthol-2-sulfonate produced a ρ of 3.05.

Previous workers have shown that there is a correlation between molecular structure and reactivity in substituted benzenediazonium cations. Kazitsyna, Kikot′, and Ashkinadze[1] reported that a linear relationship exists between the N–N stretching frequency and the Hammett substituent constant, σ, for singly substituted benzenediazonium cations and they explained this structural effect in terms of resonance theory. Increased resonance interaction between the benzene ring and the diazonium group will lower the N–N bond order,[2] and the bond-order frequency dependence is well known in other systems. Berthier, Pullman, and Pontis[3] report a linear correlation between bond order and the carbonyl stretching frequency. The same dependence is found in the P–O system.[4] A carbonyl stretching frequency and Hammett σ constant relationships have been reported by Flett[5] and Jones[6] and other frequency *vs.* σ constant correlations are summarized by Jaffé.[7]

Therefore, we can expect to determine the effective σ constant for multiple substituted derivatives by this direct measurement. Furthermore, since Zollinger[8] has shown that the coupling rate constants of single substituted benzenediazonium salts with 6-naphthol-2-sulfonate can be correlated by a Hammett ρ–σ treatment, we can check the consistency of these independent assignments by a similar correlation. Eleven

---

[1] L. A. Kazitsyna, B. S. Kikot′, L. D. Ashkinadze, and O. A. Revtov, translated from *Dokl. Akad. Nauk SSSR*, **151**, No. 3, 573 (1963).

[2] K. B. Whetsel, G. F. Hawkins, and F. E. Johnson, *J. Am. Chem. Soc.*, **78**, 3360 (1956).

[3] G. Berthier, B. Pullman, and J. Pontis, *J. Chim. Phys.*, **49**, 367 (1952).

[4] (a) J. Kumamoto, *Spectrochim. Acta.*, in press; IBM Report RJ 302; (b) E. L. Wagner, *J. Am. Chem. Soc.*, **85**, 161 (1963).

[5] M. St. C. Flett, *Trans. Faraday Soc.*, **44**, 767 (1948).

[6] R. N. Jones, W. F. Forbes, and W. A. Mueller, *Can. J. Chem.*, **35**, 504 (1957).

[7] H. H. Jaffé, *Chem. Rev.*, **53**, 214 (1953).

[8] H. Zollinger, *Helv. Chim. Acta*, **36**, 1730 (1953); "Azo and Diazo Chemistry," Interscience Publishers Inc., New York, N. Y., 1961, p. 242.

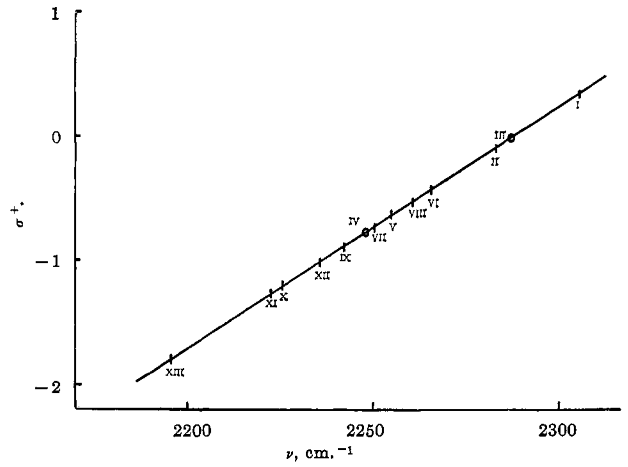


Figure 1.—Assignment of σ^+ constants.

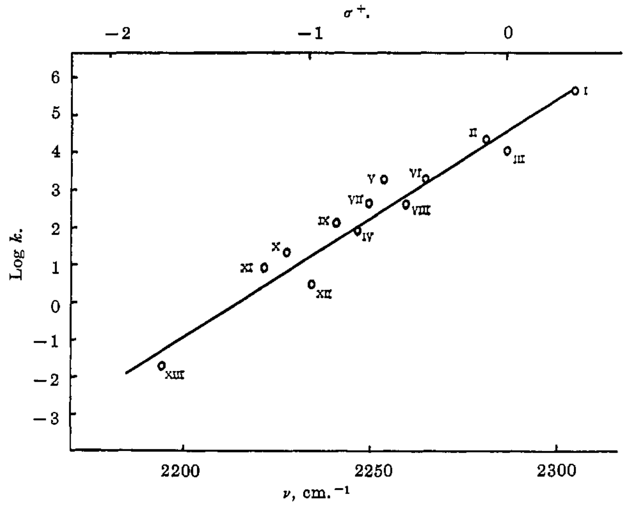


Figure 2.—Coupling rate constant *vs.* the N–N frequency (below) and σ^+ (above).

methoxy-substituted benzenediazonium fluoroborates were prepared and used to verify this independent method for determining σ constants.

Results

The observed N–N stretching frequencies for the diazonium group in the three solvent systems, dimethyl sulfoxide, dimethyl sulfoxide–water, and water, are listed in Table I. The frequencies used in the correlation were those obtained in pure water except for VI, 2,3,5-trimethoxybenzenediazonium fluoroborate, which was unobservable and so the dimethyl sulfoxide–water frequency was used.

The σ^+ constants were determined by drawing a straight line between the benzenediazonium cation at $\sigma^+ = 0$ and the 4-methoxybenzenediazonium cation at $\sigma^+ = -0.76$[9] with their observed frequencies plotted on the abscissa. The intersection of other N–N stretching frequencies with this straight line was used to assign the σ^+ constants from the ordinate, Figure 1, and these results are listed in Table II under assigned σ^+

The second-order coupling rate constants of these diazonium cations with 6-naphthol-2-sulfonate are listed in Table III and a general correlation of these

TABLE I

INFRARED ABSORPTION FREQUENCIES FOR THE N–N STRETCHING MODE (CM.⁻¹)

Benzenediazonium derivative		Solvent: Dimethyl sulfoxide	Solvent: Dimethyl sulfoxide–water	Solvent: Water
I,	4-nitro	2311	2306	2305 (w)
II,	3-methoxy	2293	2282	2283 (w)
III,	unsubstituted	2296	2288	2287 (w)
IV,	4-methoxy	2260	2248	2248
V,	3,4,5-trimethoxy	2265	*a*	2255 (w)
VI,	2,3,5-trimethoxy	2279	2265	*b*
VII,	2,5-dimethoxy	2263	2246	2250
VIII,	2-methoxy	2272	2266	2260
IX,	3,4-dimethoxy	2256	*a*	2242
X,	2,4,5-trimethoxy	2228	2227	2225
XI,	2,4-dimethoxy	2226	2223	2222
XII,	2,6-dimethoxy	2239	2236	2235
XIII,	2,4,6-trimethoxy	2215	*a*	2195

[a] Not determined. [b] Unobservable.

TABLE II

σ CONSTANTS FROM INFRARED FREQUENCIES

Benzenediazonium compound	σ^+ (Brown and Okamoto)	Assigned σ^+	$\Sigma\sigma^+$	$\Delta\sigma^+$
I	0.79	0.35		
II	0.05	−0.08		
III	0.00			
IV	−0.76			
V		−0.63	−0.92	0.29
VI		−0.43	−0.69	0.26
VII		−0.72	−0.61	−0.11
VIII		−0.53		
IX		−0.88	−0.84	−0.04
X		−1.21	−1.37	0.16
XI		−1.27	−1.29	0.02
XII		−1.01	−1.06	0.05
XIII		−1.99	−1.82	−0.17

TABLE III

KINETIC DATA

Diazonium salt	Temp., °C.	Buffer used[a]	k_1, sec.⁻¹ (obsd. pseudo-first-order × 10^4)	k_2, l./mole sec. (calcd. second-order at 27°)
I	27	A	131	5.89×10^5
II	27	A	4.70	2.74×10^4
	36	A	11.4	
	40	A	18.1	
III	27	A	2.00	1.16×10^4
IV	27			100.0[b]
	30	C	2.86	
	32	C	3.42	
	36	C	4.35	
V	27	C	52.5	2.26×10^3
	37	A	3.7	
	40	A	4.15	
VI	27	C	16.7[c]	2.16×10^3
	33	C	21.8[c]	
	41	C	49.6[c]	
VII	27	C	3.52[c]	4.58×10^2
	32	C	7.11[c]	
	42	C	16.6[c]	
VIII	27			4.35×10^2 [b]
	31	B	4.68	
	35	B	5.43	
	40	B	8.05	
IX	27	C	3.80	1.64×10^2
X	27	D	17.9	21.7
XI	27	D	7.54	9.15
XII	27			2.85[b]
	31	D	3.30	
	36	D	5.05	
	39.5	D	7.36	
XIII	27	E	0.392[d]	4.15×10^{-2}

[a] See Table V. [b] Extrapolated values. [c] 1.0 ml. of naphthol solution was used. [d] 5.0 ml. of naphthol solution was used.

---

[9] H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **79**, 1915 (1957).

rate constants with their N–N stretching frequencies is shown in Figure 2.

Discussion

The reported[10] characteristic region for the N–N stretching mode for aryldiazonium salts is around 2261 cm.$^{-1}$. Since water has approximately 15% transmission in this region when used with Irtran windows and a 14-μ silver spacer, we can observe the absorption spectrum in this thin cell owing to the unusual infrared intensity[1] of the diazonium stretching mode. The systematic behavior of the position of this absorption band with structure can be expected to correlate with coupling rate constants because a lowered stretching frequency is indicative of increased resonance interaction and this not only lowers the energy of the reactant, but also reduces the electrophilicity of the reactive end of the molecule by a more extensive delocalization of positive charge. This trend is evident from the plot in Figure 2. The behavior of the di-*ortho*-substituted derivatives, XII and XIII, indicates the absence of a steric effect. When a reaction involves an α atom, a single *ortho* substituent appears to show a steric effect,[11] but in this case, the reacting center is two atoms removed.

We have assigned σ^+ values to all the compounds examined based on a single value for the 4-methoxy group taken from Brown and Okamoto.[9] The effect of changing electron demand in different systems has been discussed in detail by Wells,[12] and an argument against a unique set of σ^+ constants is substantiated. Therefore, the more negative value of 3-methoxy and 4-nitro assigned here can be rationalized as resulting from the specific electron demand of the diazonium group. Using the assigned constants for 3-methoxy and 2-methoxy, the arithmetic sums of the monosubstituted σ^+ constants are shown in Table II, in the column under $\Sigma\sigma^+$. The difference between this and the assigned values for multiple substituted derivatives is listed in the next column under $\Delta\sigma^+$. The two largest values for $\Delta\sigma^+$, V and VI, appear where a directly conjugated methoxy group becomes sandwiched between two other groups. Their deviation is in the expected direction for a steric inhibition of resonance. In three examples, IX, XI, and XII, the agreement is quite good and in three others, VII, X, and XIII, the difference is not greater than 16%.

Conclusions

The independent determination of the proper σ^+ constants for multiple substituted diazonium fluoroborates by an infrared method has been shown to be practical by a Hammett ρ–σ correlation of the rate constants of a coupling reaction of these salts. These σ^+ constants are related to the thermodynamic stability of these molecules: the more negative the constant, the more stable the molecule. Jaffé has shown that σ constants for multiple substituted compounds obey a sum rule[13] and the data presented here are in reasonable agreement with this. Since the coupling reaction shows no steric hindrance, we conclude that a reaction at a center two atoms removed from the benzene ring, as well as geometrical changes about the N-N group owing to rehybridization along the reaction coordinate, are not sterically hindered by di-*o*-methoxy groups.

Experimental Section

Materials.—*o*-, *m*- and p-anisidine were from Eastman Organic Chemicals (White Label) and were used without further purification. 2,4-Dimethoxy-, 3,4-dimethoxy-, and 3,4,5-trimethoxyaniline were obtained from Aldrich Chemicals and were also used without further purification.

2,6-Dimethoxyaniline was prepared by the method given by Simada and Hata.[14] 2,4,6-Trimethoxyaniline was prepared by the method given by Fukui, Kuwahara, Saheki, and Mori.[15] 2,3,5-Trimethoxyaniline was prepared by the method given by Richtzenhain and Nippus.[16]

2,4,5-Trimethoxyaniline was prepared by the reduction of 2,4,5-trimethoxynitrobenzene, obtained from the method given by Quelet and Ezz.[17] 2,4,5-Trimethoxynitrobenzene (21.3 g., 0.1 mole) was dissolved in 250 ml. of 2-propanol and reduced in a Parr low-pressure hydrogenator using a palladium-on-carbon catalyst and an initial hydrogen pressure of 50 p.s.i. The reaction was completed in 30 min. and the free amine was isolated after filtering by evaporation of the solvent. The amine was recrystallized from ethanol and gave a 43% yield with a melting point of 91°.

Anal.[18] Calcd. for $C_9H_{13}NO_3$: C, 58.7; H, 7.36; N, 7.74. Found: C, 59.2; H, 7.10; N, 7.65.

The diazonium fluoroborates were prepared by the following general procedure.[19] The amine (0.2 mole) was dissolved or slurried with 10 ml. of concentrated hydrochloric acid and 25 ml. of water. This was cooled to 0° in an ice–salt bath, and stirred while 4 ml. of 5 *N* sodium nitrite was added dropwise at a rate which kept the temperature between 0 and 5°. The resulting diazonium chloride solution was filtered and 5 ml. of 48% fluoroboric acid was then added. The diazonium fluoroborate salts precipitated after several minutes and were separated by filtration. The salts were recrystallized and the solvents used are listed with the physical data in Table IV.

4-Nitrobenzenediazonium fluoroborate was Yellow Label from Eastman Organic Chemicals and used directly.

Benzenediazonium fluoroborate was prepared by the general method used above.[19]

Sodium 6-naphthol-2-sulfonate, technical grade reagent from Eastman Organic Chemicals, was treated with Darco and twice recrystallized from water before use.

Buffer solutions were made up as described by Zollinger[8] and Fieser[20] and each pH was measured with a Beckman Model G pH meter. The ionic strength was adjusted to 0.25 by the addition of potassium chloride. The details can be found in Table V.

Infrared Spectra.—The spectra were recorded with a Perkin-Elmer Model 521 spectrophotometer at ambient temperatures. A 20 cm.$^{-1}$/in. chart-scale expansion was used in the region 2400 to 2000 cm.$^{-1}$. Spectra using dimethyl sulfoxide as solvent were obtained in a 0.1-mm. rock salt cavity cell with a solvent wedge compensator. The dimethyl sulfoxide–water and water spectra were obtained using Irtran windows with a 14-μ silver spacer and a neutral density in the reference beam.

Kinetic Method.—A thermostated cell holder similar to that described by Bell and Stryker,[21] but modified for a Cary Model 14, was used to carry out the kinetic runs *in situ*. The cell-holder temperature was regulated by a glycol bath controlled with a Bronwill constant-temperature circulator. The same coupling

---

[10] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1964, p. 273.

[11] G. G. Smith and B. L. Yates, *J. Org. Chem.*, **30**, 434 (1965).

[12] P. R. Wells, *Chem. Rev.*, **63**, 188 (1963).

[13] H. H. Jaffé, *ibid.*, **53**, 243 (1952).

[14] T. Simada and K. Hata, *Sci. Papers Inst. Phys. Chem. Res.* (Tokyo), **35**, 365 (1939).

[15] T. Fukui, Y. Kuwahara, K. Saheki, and M. Mori, *Yakugaku Zasshi*, **80**, 1472 (1960), *Chem. Abstr.*, **55**, 5395 (1961).

[16] H. Richtzenhain and P. Nippus, *Ber.*, **82**, 408 (1949).

[17] R. Quelet and A. A. Ezz, *Bull. soc. chim. France*, **26**, 349 (1959).

[18] Analyses were by the Berkeley Microanalytical Laboratory, Berkeley, Calif.

[19] E. Wilke-Dörfurt and G. Balz, *Ber.*, **60**, 115 (1927).

[20] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1957, inside back cover.

[21] P. H. Bell and C. R. Stryker, *Science*, **105**, 415 (1947).

TABLE IV

SUMMARY OF THE PHYSICAL CONSTANTS OF THE DIAZONIUM SALTS

Amine used	Yield of diazonium fluoroborate, %	Recrystn. solvent	Dec. temp., °C. (uncor.)	% C[a] Calcd.	% C[a] Found	% H[a] Calcd.	% H[a] Found	% N[a] Calcd.	% N[a] Found
o-Anisidine[b]	40	Methanol	95–97	37.9	37.5	3.16	3.33	12.6	12.4
m-Anisidine[c]	30	Methanol	80–81	37.9	38.0	3.16	3.44	12.6	12.4
p-Anisidine[d]	72	Methanol	143	37.9	38.0	3.16	3.39	12.6	12.6
2,4-Dimethoxyaniline	40	Methanol	*e*	38.2	38.5	3.58	3.62	11.1	11.3
2,5-Dimethoxyaniline	55	Methanol–ether	109	38.2	37.9	3.58	3.53	11.1	11.2
2,6-Dimethoxyaniline	52	Methanol	*e*	38.2	38.2	3.58	3.67	11.1	11.1
3,4-Dimethoxyaniline	60	Methanol	116	38.2	38.4	3.58	3.58	11.1	11.1
2,4,6-Trimethoxyaniline	62	Water	*e*	38.4	37.8	3.91	3.94	9.95	9.98
2,3,5-Trimethoxyaniline	65	Methanol	127	38.4	38.4	3.91	3.88	9.95	10.2
3,4,5-Trimethoxyaniline	62	Methanol–water	116	38.4	38.6	3.91	3.95	9.95	10.2
2,4,5-Trimethoxyaniline	74	Ethanol–water	*e*	38.4	38.4	3.91	3.83	9.95	9.92

[a] Footnote 18. [b] G. Schiemann and M. Seyhan, *Ber.*, **70**, 2396 (1937). [c] B. C. Berker and R. Adams, *J. Am. Chem. Soc.*, **54**, 2973 (1932). [d] A. Roe, *Org. Reactions*, **5**, 205 (1957). [e] Not determined.

TABLE V

BUFFER SOLUTIONS MEASURED AT 27° AND $\mu = 0.25$

	pH	Components (g./l.)
A	4.27	$CH_3CO_2Na \cdot 3H_2O$ (1.3), CH_3CO_2H (0.60), KCl (18.9)
B	5.95	KH_2PO_4 (23.2), Na_2HPO_4 (4.3), KCl (3.7)
C	6.40	$Na_2HPO_4 \cdot 12H_2O$ (1.8), $Na_2HPO_4 \cdot 2H_2O$ (1.5), KCl (16.7)
D	7.95	Boric acid (11.8), borax (9.1), KCl (3.7)
E	9.08	Boric acid (6.2), borax (38.1), KCl (3.7)

$$k_1 \text{ (observed)} = k_2 \text{ (diazonium) (naphtholate anion)} \qquad (1)$$

$$\frac{\text{(naphtholate anion) (H}^+\text{)}}{\text{(naphthol)}} = K_{\text{equil}} \qquad (2)$$

system that was described by Zollinger[8] to obtain pseudo-first-order rate constants was used in these experiments, except that the actual rate data were obtained by a continuous measurement of the optical density of the dyes formed. We followed Zollinger's method for evaluating the true second-order rate constant from the observed first-order rate constant. The first-order rate constant, k_1, comes from a coupling reaction where the concentration of the coupler is kept relatively constant in a buffer-controlled equilibrium. The second-order constant can be calculated from the preceding relationships (eq. 1 and 2). The appropriate amount of diazonium salt was dissolved in water such that a 1.0-ml. aliquot would produce enough dye to give a final optical density of approximately 2.0 in the 5000-Å. region. This aliquot and 3.0 ml. of .012 *M* sodium 6-naphthol-2-sulfonate were added to 26 ml. of buffer solution. The final ionic strength was 0.22. The kinetic data were analyzed by taking the final optical density as proportional to the initial diazonium ion concentration and ($O.D._\infty - O.D._t$) as proportional to the diazonium concentration at any time, *t*. Clean, first-order plots were obtained in all cases. The details of the individual kinetic runs are given in Table III.

The Preparation and Properties of Some Salts of 2,2-Diphenylcyclopropyldiazonium Hydroxide[1]

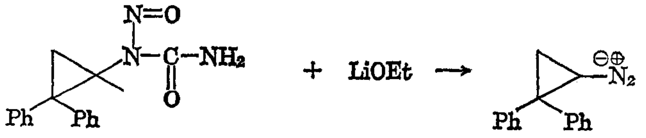
T. K. TANDY, JR., AND W. M. JONES[2]

Department of Chemistry, University of Florida, Gainesville, Florida

Received May 10, 1965

In the course of our investigation of the base-induced decomposition of N-nitroso-N-(2,2-diphenylcyclopropyl)-urea, we have succeeded in isolating several salts of 2,2-diphenylcyclopropyldiazonium hydroxide. The methods of preparation of this unusual and interesting type of compound are discussed as are their reactions with acylating agents and benzoic acid.

In the course of our investigations on the base-induced conversion of N-nitroso-N-(2,2-diphenylcyclopropyl)urea to 2,2-diphenyldiazocyclopropane,[3,4] we have succeeded in isolating several salts of 2,2-diphenylcyclopropyldiazonium hydroxide (III).



I II

The purpose of this paper is to report the method of synthesis of this interesting and relatively rare type of molecule[5] and to report some of the chemical properties of these salts that do not relate directly to the course of the conversion of N-nitroso-N-(2,2-diphenylchloropropyl)urea to 2,2-diphenyldiazocyclopropane. In another paper,[4] we reported the properties of these salts that do pertain to the mechanism of this specific reaction.

---

(1) Based upon a dissertation submitted by Thomas King Tandy, Jr. in 1964 to the Faculty of the University of Florida in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Alfred P. Sloan Fellow.

(3) *Cf.* W. M. Jones, M. H. Grasley, and W. S. Brey, Jr., *J. Am. Chem. Soc.*, **85**, 2754 (1963), and references cited therein.

(4) W. M. Jones, D. L. Muck, and T. K. Tandy, Jr., *ibid.*, in press.

(5) To the best of our knowledge, the only other aliphatic diazotates that have been reported are some salts of methyl and benzyl diazonium hydroxide.[6-9]

(6) A. Hantzsch and M. Lehman, *Ber.*, **35**, 897 (1902).

(7) J. Thiele, *Ann.*, **376**, 239 (1910).

(8) E. Mueller, W. Hoppe, H. Hagenmaier, H. Haiss, R. Huber, W. Rundel, and H. Suhr, *Ber.*, **96**, 1712 (1963); E. Mueller, W. Rundel, H. Haiss, and H. Hagenmaier, *Z. Naturforsch.*, **b15**, 751 (1960).

(9) For a general discussion on both aliphatic and aromatic diazotates, see H. Zollinger, "Azo and Diazo Chemistry, Aliphatic and Aromatic Compounds," Interscience Publishers, Inc., New York, N. Y., 1961, pp. 44–67.