crystalline, easily sublimed **4**. Spectra and analysis are in the tables.

5,5-Diphenyl-2-phenylimino-Δ^3-1,3,4-oxadiazoline (**9**).—Addition of benzophenone 4-phenylsemicarbazone (5.0 g, 0.016 mol) in 50 ml of methylene chloride to a solution of LTA (10.6 g, 0.024 mol) in 250 ml of methylene chloride at 0° caused no change in color. The temperature was raised to 30°, the solution gradually became orange, and a white precipitate was slowly formed. After 40 min, 100 ml of water was added. The work-up described above gave a dark red oil which was dissolved in the minimum volume of chloroform. The solution was diluted with 250 ml of petroleum ether (bp 30–60°) and the amorphous, brown precipitate which settled was filtered off. Concentration of the orange filtrate with a rotary evaporator gave yellow crystals which were recrystallized many times from petroleum ether–chloroform to remove traces of benzophenone azine, a contaminant of the starting material (*vide supra*). Pure **9** (1.0 g, 20%) was obtained as bright yellow prisms. For spectra, properties and analysis, see Tables I and II.

Catalytic Hydrogenation of 5,5-Dimethyl-2-benzylimino-Δ^3-1,3,4-oxadiazoline (**4**).—The title compound (0.300 g), in about 100 ml of ethanol, and 5% palladium–charcoal catalyst (0.5 g) were shaken for 3 hr at room temperature under hydrogen at 48 psi. After two filtrations most of the solvent was evaporated to leave 0.275 g (91%) of acetone 4-benzylsemicarbazone. Identity was established by comparing the infrared spectrum of the product with that of authentic material.

Thermolysis of 5,5-Diphenyl-2-phenylimino-Δ^3-1,3,4-oxadiazoline (**9**).—The title compound (0.2 g) in 50 ml of chlorobenzene was decomposed at 104.4° in an apparatus for measuring rates of gas evolution.[15] When 50% of 1 equiv of gas had evolved the flask was cooled rapidly and the solution was distilled (1 mm) at room temperature. The infrared spectrum (CCl_4) of the red, pasty residue contained sharp bands at 2270 (phenyl isocyanate), 2125 (phenyl isocyanide), 2042 (diphenyldiazomethane), 1655 (benzophenone), and 1706 cm^{-1} (unreacted oxadiazoline). These assignments are in agreement with spectral data in the literature and were confirmed as follows. Addition of 1 drop of aniline to the solution used for the ir spectrum resulted in disappearance of the absorption at 2270 cm^{-1}. Total decomposition of the oxadiazoline in petroleum ether, followed by addition of aniline and further heating led to a product with the ir spectrum of N,N′-diphenylurea. Phenyl isocyanide, from chloroform, aniline, and alcoholic KOH,[16] absorbed at 2125 cm^{-1} of the ir spectrum and matched the odor of the mixture from partial pyrolysis of the oxadiazoline. Chromatography of the petroleum ether soluble portion of the distillation residue (see above) on neutral alumina caused separation of a violet fraction having an ir spectrum identical with that of diphenyldiazomethane prepared by oxidation of the hydrazone of benzophenone. Further elution of the column gave a clear oil with ir spectrum (CCl_4) superimposable on that of authentic benzophenone.

Registry No.—**4**, 21449-51-4; **5**, 21449-52-5; **6**, 21449-53-6; **7**, 21449-54-7; **8**, 21449-55-8; **9**, 21449-56-9 **10**, 21449-57-0; **11**, 21449-58-1; **12**, 21449-59-2; lead tetraacetate, 546-67-8; acetone 4-(*p*-methoxyphenyl)-semicarbazone, 21367-45-3; acetone 4-(*p*-tolyl)semicarbazone, 21367-46-4; acetone 4-(*p*-chlorophenyl)-semicarbazone, 21367-47-5; *p,p′*-dimethylbenzophenone 4-phenylsemicarbazone, 21367-48-6; *p,p′*-dichlorobenzophenone 4-phenylsemicarbazone, 21367-49-7; *p,p′*-dimethoxybenzophenone 4-phenylsemicarbazone, 21367-50-0.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Partial support from the National Research Council of Canada, including studentships to A. M. C. and P. R. W., is also gratefully acknowledged. We are indebted to Professor D. B. MacLean for the mass spectra.

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[15] J. Warkentin, *J. Chem. Educ.*, **43**, 265 (1966).

[16] A. W. Hoffman, *Justus Liebigs Ann. Chem.*, **144**, 114 (1867).

Thermolysis of 5,5-Diaryl-2-phenylimino-Δ^3-1,3,4-oxadiazolines[1,2]

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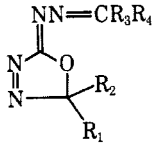
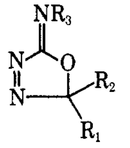
Received September 9, 1968

Thermolysis of 5,5-diaryl-2-phenylimino-Δ^3-1,3,4-oxadiazolines (**2a**–**2d**) at 104.4° in chlorobenzene may take either or both of two pathways, A and B. Path A, leading to N_2, diaryl ketone, and phenyl isocyanide is the major pathway in thermolysis of **2a**. Path B, leading to diaryldiazomethane and phenyl isocyanate, accounts for about 95% of the total reaction of **2d**. Rates of the retro-1,3-dipolar addition (path B) are correlated by means of the equation $\log k/k_0 = \rho[\sigma + r(\sigma^+ - \sigma)]$, with $r = 0.55$ and $\rho = -1.39$. Substituent effects on rates of reaction A are smaller and in the opposite sense but it is not certain that the Hammett equation is followed. Possible mechanisms for the decompositions are discussed.

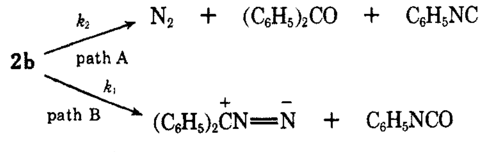
The syntheses of oxadiazolines **1**[3] and **2**[4] by oxidative cyclization of carbohydrazones and semicarbazones, respectively, of ketones were reported recently. Among properties of **2**, cited in support of the assigned structure, was the thermal decomposition of **2b** according to eq 1. This duality of pathways for breakdown of the ring system was intriguing, for it appeared to represent a delicate balance between conventional decomposition of a cyclic azo compound (initial loss of N_2) and the reverse of a 1,3-dipolar cycloaddition reaction, path B. This report is concerned with a kinetic study of the



1



2a, $R_1 = R_2 = p\text{-}C_6H_4Cl$; $R_3 = C_6H_5$
b, $R_1 = R_2 = R_3 = C_6H_5$
c, $R_1 = R_2 = p\text{-}C_6H_4CH_3$; $R_3 = C_6H_5$
d, $R_1 = R_2 = p\text{-}C_6H_4OCH_3$; $R_3 = C_6H_5$



(1)

$$(C_6H_5)_2\overset{+}{C}N{=}\overset{-}{N} \xrightarrow{k_3} (C_6H_5)_2C{:} + N_2 \qquad (2)$$

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Research Council of Canada for financial support of this project.

[2] Taken from the Ph.D. Thesis of P. R. West, McMaster University, 1967.

[3] P. R. West and J. Warkentin, *J. Org. Chem.*, **33**, 2089 (1968).

[4] A. M. Cameron, P. R. West, and J. Warkentin, *ibid.*, **34**, 3230 (1969).

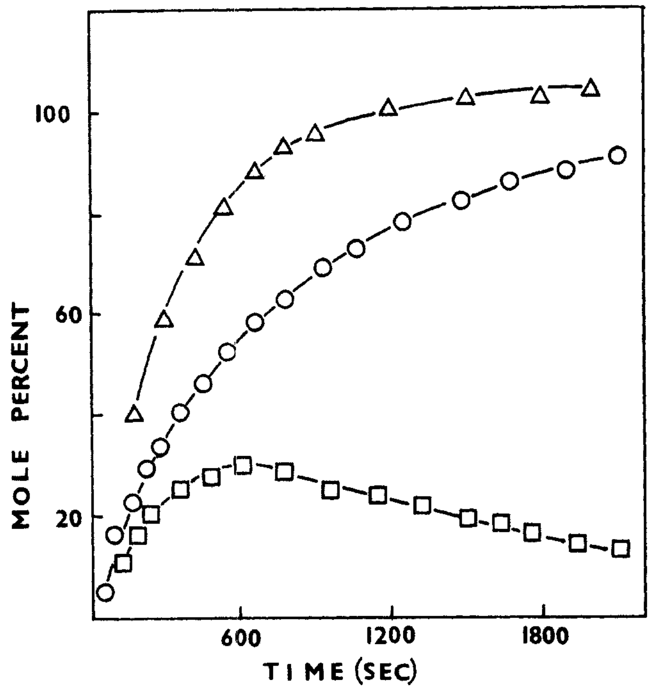
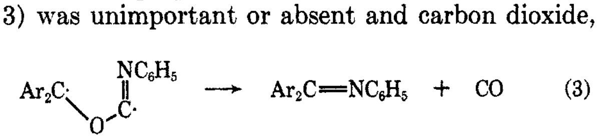


Figure 1.—Kinetics of decomposition of **2b** in C_6H_5Cl: diphenyldiazomethane in solution, □; gas evolved, ○; diphenyldiazomethane plus gas, △.

reactions, aimed at elucidating some of the mechanistic detail.

Methods and Results

Products.—The kinetics and stoichiometry of gas evolution were determined by heating solutions of oxadiazolines (*ca.* 10^{-2} *M* in C_6H_5Cl) at constant pressure until the volume remained constant (see Experimental Section). The yield of gas was 1 equiv within experimental error and it was all nitrogen as indicated by the material balance on oxadiazoline oxygen (*vide infra*). Carbon monoxide, from a process similar to that proposed to explain the mass spectra[3,4] (eq 3) was unimportant or absent and carbon dioxide,



$$Ar_2C(NC_6H_5)(O)C\cdot \longrightarrow Ar_2C{=}NC_6H_5 + CO \quad (3)$$

from bimolecular thermal decomposition of phenyl isocyanate (eq 4), could also be excluded. The latter reaction has been observed,[5] although at a much higher temperature (200°).

$$2C_6H_5N{=}C{=}O \longrightarrow C_6H_5N{=}C{=}NC_6H_5 + CO_2 \quad (4)$$

Diaryldiazomethanes were identified in partly decomposed oxadiazoline solutions by isolation and comparison of infrared spectra with those of materials synthesized separately.[4] Aryl isocyanides and isocyanates were identified by infrared.[4] Phenyl isocyanate was also converted into diphenylurea by reaction with aniline. Diaryl ketones were isolated and characterized by comparison with the samples from which the oxadiazolines were first prepared.[4] Ketone plus isocyanate accounted for all the oxadiazoline ring oxygen.

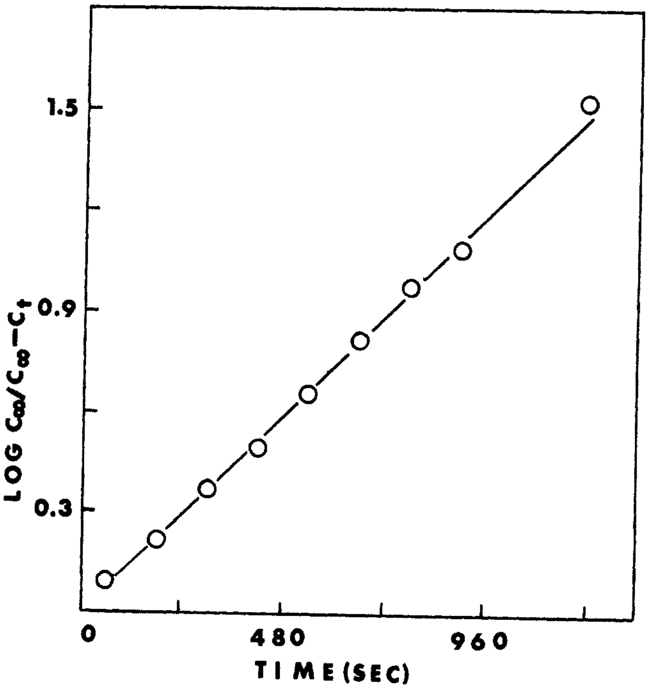


Figure 2.—Total rate of decomposition of **2b** in C_6H_5Cl at 104.4°.

No attempt was made to elucidate all of the fates of the diarylcarbene, eq 2. Ketenimine formation (eq 5) was inferred from the gradual fall in isocyanide concentration in the later stages of decomposition of oxadiazoline **2b** and from the appearance of an absorption band at 2000 cm^{-1} in the infrared.[6]

$$C_6H_5NC + (C_6H_5)_2C: \longrightarrow C_6H_5N{=}C{=}C(C_6H_5)_2 \quad (5)$$

Kinetics.—For parallel, first-order reactions with a consecutive, first-order reaction superimposed (eq 1 and 2) the rate constants are related to the maximum concentration of unstable intermediate (here Ar_2CN_2) through eq 6,[7] in which $a = k_1 + k_2$, the total first-

$$[Ar_2CN_2]_{max} = \frac{k_1}{a}\left(\frac{k_3}{a}\right)^{\left(\frac{k_3/a}{1 - k_3/a}\right)} \quad (6)$$

order rate constant for oxadiazoline decomposition. The latter was obtained by plotting log $C_\infty/(C_\infty - C_t)$ against time, where the terms C represent the sum, in mole fraction units, of nitrogen evolved and diazoalkane in solution, at the time indicated by the subscript. The mole fraction of nitrogen gas as a function of time was obtained from the gas evolution experiment, in which the starting oxadiazoline concentration was about 9×10^{-3} *M*. The mole fraction of diaryldiazomethane as a function of time was determined by analyzing aliquots from a more concentrated starting solution (*ca.* 8×10^{-2} *M* oxadiazoline in C_6H_5Cl) by infrared, using a calibration curve established independently for each diazoalkane. These decompositions were carried out in stoppered test tubes with air above the solutions. Control experiments showed that evaporation of solvent during the sampling time was negligible.

Figure 1 consists of typical plots of mole per cent N_2, mole per cent diazoalkane, and the sum of these quantities, *vs.* time. The total first-order rate constant

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[5] T. W. Campbell, J. J. Monagle, and V. S. Foldi, *J. Amer. Chem. Soc.*, **84**, 3673 (1962).

[6] D. H. Williams and I. Fleming, "Spectroscopic Methods in Organic Chemistry," McGraw-Hill Book Co., London, 1966, p 59.

[7] N. M. Rodiguin and E. N. Rodiguina in "Consecutive Chemical Reactions," Engl. ed, R. F. Schneider, Ed., D. Van Nostrand Co., Toronto, 1964, Chapter 5.

TABLE I

THERMOLYSIS OF 5,5-DIARYL-2-PHENYLIMINO-Δ^3-1,3,4-OXADIAZOLINES IN CHLOROBENZENE AT 104.4°

Compd	$[Ar_2CN_2]_{max}$, mol %	Rate constants × 10^3, sec^{-1} [a]				
		$k_1 + k_2$	k_1	k_2	k_3[b]	k_3[c]
2a	10.2 ± 1.5	4.00 ± 0.01	0.61 ± 0.13	3.39 ± 0.13	0.83 ± 0.11	...[d]
2b	31.1 ± 0.5	2.93 ± 0.15	1.45 ± 0.12	1.48 ± 0.12	0.76 ± 0.08	0.91 ± 0.03
2c	62.0 ± 0.9	9.01 ± 0.35	7.81 ± 0.31	1.20 ± 0.20	1.36[e]	1.39 ± 0.03
2d	95.1 ± 3.3		34.7 ± 6.5[f]			
			2.71 ± 0.25[g]			
			0.67 ± 0.01[h]			
			0.0242[i]			

[a] Errors are standard devations, except as indicated. [b] From diazoalkane concentration, by infrared. [c] From nitrogen evolution data. [d] Gas evolution method not usable. Not enough N_2 is evolved from Ar_2CN_2 after all of the oxadiazoline has decomposed. [e] Single determination. [f] Extrapolated to 104.4°. The error limits are calculated from the extreme slopes of Figure 3. [g] At 73.4°. [h] At 58.8°. [i] At 49.3°, single determination.

was obtained by plotting the data for the upper curve of Figure 1 in first-order form (Figure 2) and by applying the equation 2.303 × slope = $k_1 + k_2$.

The infrared data gave, in addition to $[Ar_2CN_2]_{max}$, values of the rate constants (k_3) for decomposition of diaryldiazomethanes. After decomposition of a given oxadiazoline was essentially complete, the concentration of the corresponding diazoalkane fell with first-order kinetics. Gas evolution data for the later part of a run also represent decomposition of diazoalkane alone and provide a check on the infrared-derived value of k_3. In the two cases where a comparison was possible, agreement between the values of k_3 from the two sources was within 3% (**2c**) and 18% (**2b**), Table I. Since **2b** gives only half the maximum diazoalkane concentration observed for **2c** (31 and 62 mol %, respectively) the poorer agreement in the case of **2b** probably comes from error in the gas-evolution value of k_3. The method is not very reliable for small amounts of evolved gas. Values from the infrared measurements were used in all cases, a choice suggested also by the agreement between our value of k_3 and that calculated (7.50×10^{-4} sec^{-1}) for decomposition of diphenyldiazomethane in xylene at the same temperature.[8]

Values of $k_1 + k_2$, $[Ar_2CN_2]_{max}$, and k_3, obtained as described, suffice for evaluation of k_1 and k_2 from eq 6. Oxadiazoline **2d** was a special case. It decomposed quite cleanly *via* path B alone but too rapidly at 104.4°. Its thermolysis was followed at three lower temperatures (Table I), at which di-*p*-methoxyphenyldiazomethane is relatively stable, so that the maximum concentration of the latter came close to 100 mol %. The data fitted scheme B (eq 1) alone very well and k_1 values, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (Figure 3) were obtained by the usual method for simple, first-order reactions. The rate constant at 104.4° was then calculated from the activation parameters. Table I lists the rate data.

Discussion

There are several reasons for assuming that the first-order processes of eq 1 and 2 describe the systems adequately. The good first-order fits (Figure 2) obtained by summing data from two different experiments suggest that the rates are insensitive to substrate concentration, oxygen concentration,[9] and product concentration over the limits within which these parameters varied (*vide supra*). Solvent purity was also not critical. A good grade of chlorobenzene could be used without the purification procedure that was normally followed (see Experimental Section) without affecting rates. Addition of 1 ml of aniline to 50 ml of the solvent did not alter the rate of thermolysis of **2b** appreciably. Thus it is likely that the rate constants in Table I are true unimolecular constants and not pseudo-first-order constants of processes catalyzed by traces of impurities.

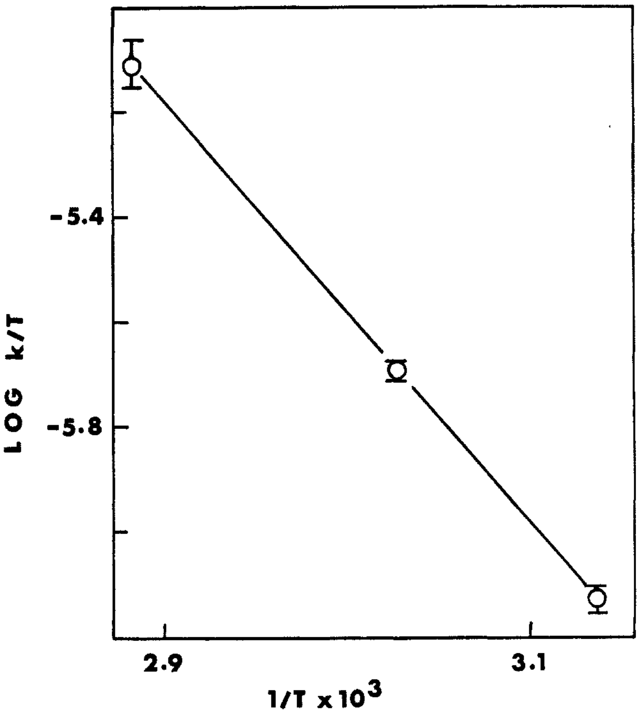

Figure 3.—Plot for determination of activation parameters for thermolysis of **2d** in C_6H_5Cl.

The data in Table I indicate that substituents in the ring phenyl groups have a strong influence on the k_1/k_2 ratio, *i.e.*, on the decomposition pathway of choice. A Hammett correlation of the retro-1,3-dipolar addition process (k_1 values) was unsuccessful with either σ constants or σ^+ constants but a linear plot was obtained through use of the modified Hammett relationship,[10,11] eq 7, with $r = 0.55$. The reaction constant ρ has the value −1.39 (Figure 4) with correlation coefficient 0.99.

$$\log k/k_0 = \rho[\sigma + r(\sigma^+ - \sigma)] \qquad (7)$$

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[8] G. Murgulescu and T. Oncescu, *J. Chim. Phys.*, **58**, 508 (1961).

[9] Oxygen was excluded in the gas-evolution runs, of course, because consumption of O_2 would appear to reduce the rate of evolution of N_2 as well as the yield.

[10] Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Jap.*, **32**, 965 (1959).

[11] Y. Yukawa and Y. Tsuno, *ibid.*, **32**, 971 (1959).

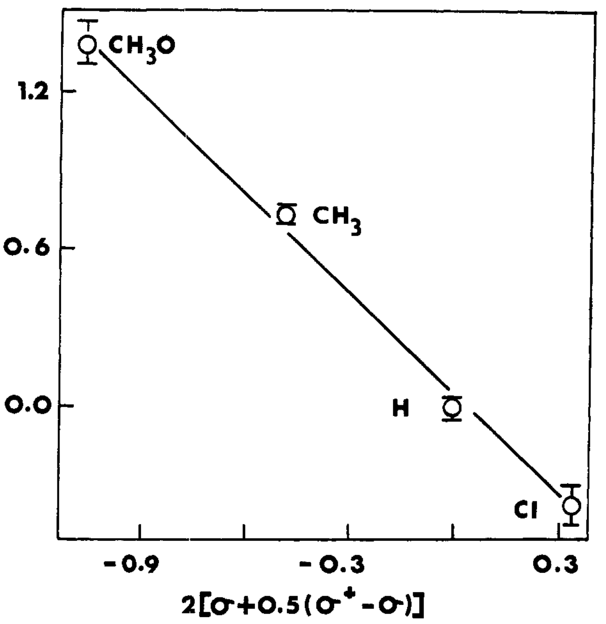
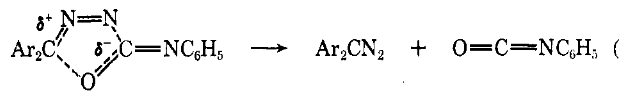


Figure 4.—Modified Hammett plot for retro-1,3-dipolar cycloaddition (path B) of oxadiazololines **2a–2d**.

A need for mixing substituent constants to correlate rates has been demonstrated in other reactions of the cycloaddition type. For comparison, the Diels–Alder reaction of *p*-substituted 1-phenylbutadienes with maleic anhydride in dioxane[12] is correlated[11] by means of eq 7 with $r = 0.475$ and $\rho = -0.711$ at 45°. In the case of the oxadiazolines, the type of fit and the magnitude of ρ make it very probable that C—O bond breaking is the rate-determining step of reaction B (eq 1), if the reaction is stepwise. However the substituent effects are also plausible for concerted reaction (eq 8) through a polar transition state.



(8)

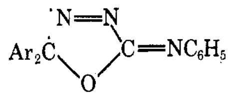
The activation parameters for decomposition of **2d** ($\Delta H^{\ddagger} = 20.1 \pm 1.3$ kcal mol^{-1}, $\Delta S^{\ddagger} = -13.1 \pm 4.0$ eu) do not provide the answer as the entropy of activation for the polar process is probably dominated by a contribution from solvent electrostriction. The sign and magnitude of $\Delta S^{\ddagger}$ are plausible then for either a stepwise or a concerted process.

Huisgen[13,14] has interpreted a large body of evidence in favor of the concerted mechanism for 1,3-dipolar cycloadditions. The same evidence has also been held to be in equally good or better accord with the stepwise mechanism.[15] In view of this controversy regarding the detailed mechanism of the forward reaction, that of the reverse process (path B, eq 1) must be equally unsettled at this time.

The reverse of path B is not a known process. It was ruled out in the present study by mixing diphenyldiazomethane with phenyl isocyanate in chlorobenzene at 104° in the dark. Although the concentrations used were higher than those encountered during decomposition of oxadiazoline **2b**, neither benzophenone nor phenyl isocyanide could be detected after all of the diazoalkane had decomposed. Aryl isocyanates do react with 1,3 dipolarophiles, both thermally[16] and photochemically,[17] but addition occurs to the N=C bond instead of the C=O bond. In the systems considered here, addition to C=N was also undetected for, in infrared runs on oxadiazolines, the isocyanate concentration reached a constant value with diazoalkane still present.

The Hammett treatment was also applied to reaction A of eq 1. Only three points were available, for **2d** did not decompose by path A. The fit to a straight line is poor and it is not clear whether the Hammett equation is followed. There is no doubt, however, that the reaction responds in the opposite sense to substituents and that it is less sensitive to substituents than path B.

With the limited data available it is not possible to say much about the mechanism of reaction A, except that it is probably a homolytic process in which C_5—N bond breaking is part of the rate-determining step. Further experiments are required to determine whether there are intermediates such as **3** and **4**. Attempts to capture intermediates by running decompositions in neat cyclohexene were unsuccessful.



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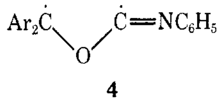

4

The effect of electron-withdrawing substituents on rates of reaction A can be accounted for in terms of a ground-state inductive effect similar to that postulated to explain the thermolysis rates of 4,4′-disubstituted benzoyldimides,[18] eq 9. In that system the rates are

$$XC_6H_4CON{=}NCOC_6H_4X \longrightarrow 2XC_6H_4\dot{C}O + N_2 \qquad (9)$$

in the order $k_{X\,=\,Cl} > k_{X\,=\,CH_3} > k_{X\,=\,CH_3O}$, an order attributed to ground-state effects on the C—N bond strength.[18] Concerted decomposition, which is allowed according to orbital symmetry theory,[19] is another mechanistic possibility for path A.

Experimental Section

Oxadiazolines 2a–2d.—The syntheses of these compounds and their properties are reported elsewhere.[4]

Chlorobenzene Solvent.—Certified Reagent Grade chlorobenzene from Fisher Scientific was shaken with successive portions of concentrated sulfuric acid until the acid layer no longer became pale yellow. After washes with several portions of water, bicarbonate solution, and again with water, the solvent was dried over calcium chloride and distilled. The middle fraction, bp 131.5–132.5°, was collected.

After it was established that the above purification procedure could be omitted without affecting rate constants, Reagent Grade chlorobenzene, from either Fisher Scientific Co., or Eastern Chemical Co. was used directly.

Gas-Evolution Kinetics.—The apparatus consisted of a vacuum line with calibrated, thermostated, 50-ml buret, leveling bulb, mercury manometer, pumping lead, gas inlet, and ball-joint terminal for connection to the reaction vessel. Unthermostated sections of the line were made from a 2-mm capillary, and

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[12] E. J. DeWitt, C. T. Lester, and G. A. Ropp, *J. Amer. Chem. Soc.*, **78**, 2101 (1956).

[13] R. Huisgen, *Angew. Chem.*, **75**, 742 (1963).

[14] R. Huisgen, *J. Org. Chem.*, **33**, 2291 (1968).

[15] R. A. Firestone, *ibid.*, **33**, 2285 (1968).

[16] R. Grashey and K. Adelsberger, *Angew. Chem.*, **74**, 292 (1962).

[17] J. C. Sheehan and I. Lengyel, *J. Org. Chem.*, **28**, 3252 (1963).

[18] J. E. Leffler and W. B. Bond, *J. Amer. Chem. Soc.*, **78**, 335 (1956).

[19] For recent reviews, see (a) R. Hoffman and R. B. Woodward, *Accounts Chem. Research*, **1**, 17, 1968; (b) G. B. Gill, *Quart. Rev.*, **22**, 338 (1968).

flared sections near stopcocks were wrapped with glass wool. The reaction vessel, fitted with top-driven magnetic stirrer, has been described elsewhere.[20]

In a typical run the vessel was charged with 50 ml of chlorobenzene which was then degassed by means of several freeze–pump–thaw cycles. Oxygen-free nitrogen or helium was admitted to a pressure below 1 atm and the flask was placed into the constant-temperature oil bath. Stirring at 2000 rpm was begun and adjustments of the pressure were made until thermal equilibrium at one atmosphere was attained. Enough oxadiazoline to liberate about 40 ml of nitrogen, dissolved in about 1 ml of solvent, was injected through a septum by means of a syringe with a long needle. The mercury reservoir was adjusted manually to maintain atmospheric pressure while volume–time data were recorded until the volume became constant.

Rate Measurements by Infrared.—The intensity of the characteristic, isolated diazo absorption near 2040 cm^{-1} of the spectrum was measured with a Perkin-Elmer 521 instrument. Peak heights were converted to concentration figures through use of calibration curves obtained with chlorobenzene solutions prepared from pure diaryldiazomethanes. Cells were of NaCl spaced 0.1 mm.

Reaction vessels for the infrared-monitored decompositions were 20 × 200 mm test tubes. Chlorobenzene (5 ml) was pipeted into a tube which was then stoppered tightly and placed in the oil bath. When thermal equilibrium had been reached a known quantity of oxadiazoline in a little chlorobenzene was injected and the tube was shaken in the bath to mix the contents. Initial concentrations of oxadiazolines were about $8 \times 10^{-2} M$. Control experiments showed that solution temperature was within 0.5° of the bath temperature in 1 min from the time of injection.

Sampling was accomplished by removing 0.1-ml aliquots with a pipet and injecting these into ice-cold test tubes. The diazoalkane concentration was followed until it had dropped to about 10% of its maximum value, 20 to 30 points being taken.

A control experiment, in which phenyl isocyanate concentration was invariant, showed that the sampling technique did not lead to appreciable losses of solvent by evaporation.

Registry No.—**2a**, 21449-58-1; **2b**, 21449-56-9; **2c**, 21449-57-0; **2d**, 21449-59-2.

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(20) J. Warkentin, *J. Chem. Educ.*, **43**, 265 (1966).

Diazocine Chemistry. VI. An Inquiry into the Aromaticity of 5,6-Dihydrodibenzo[*b,f*][1,2]diazocine

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Received March 10, 1969

The synthesis of dibenzo[*b,f*][1,2]diazocine (**1**) and its reduction to the 5,6-dihydrodibenzo[*b,f*][1,2]diazocine (**2**) is described. The spectral properties of the latter compound indicate that its central ring, because of the presence of 10 π electrons, is somewhat resonance-stabilized.

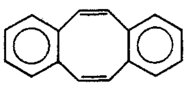
Our interest in the chemistry of nitrogen analogs of cyclooctatetraene[1] has led us to prepare dibenzo[*b,f*][1,2]diazocine (**1**) and the dihydro derivative **2**. The latter compound is of considerable interest, since it represents a potentially aromatic ring system which is isoelectronic with the dibenzo[*a,e*]cyclooctatetraene dianion.[2]

The reduction of *o,o*-dinitrobibenzyl with zinc and barium hydroxide afforded the 5,6,11,12-tetrahydrodibenzo[*b,f*][1,2]diazocine (**5**). The nmr spectrum (*cf.* Experimental Section) of this previously prepared[3] compound confirms its assigned structure (**5**). It should be mentioned that the methylene protons appear as a singlet, and consequently the central ring is not locked into a particular conformation.

The dihydro compound **5** is readily oxidized to the 11,12-dihydrodibenzo[*b,f*][1,2]diazocine (**6**),[3,4] whose structure is also confirmed by its nmr spectrum. The methylene protons now appear as an AB system, in agreement with expectation for a tub-shaped system such as is shown for this compound in Scheme I.[5]

In order to introduce the desired double bond at positions 11 to 12, the dihydro compound **6** was treated with N-bromosuccinimide to yield the monobromo dihydro derivative **7**. The nmr spectrum of this substance showed the anticipated ABX pattern due to the methine and methylene protons. This compound was readily dehydrohalogenated by treatment with potassium *t*-butoxide to afford the diazocine **1**. The structure proof of this compound, in addition to the elemental analysis, and its mass spectrometric molecular weight, rests upon the following observations.

(a) Its ultraviolet spectrum is closely similar to that of dibenzo[*a,e*]cyclooctatetraene (**3**).



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(b) The olefinic protons in compound **1** resonate within 0.01 ppm of those in dibenzo[*a,e*]cyclooctatetraene (δ 6.71).

(c) Electron bombardment causes the loss of N_2 from compound **1**.

The cited spectral data indicate that compound **1** has a geometry similar to that of the dibenzo[*a,e*]cyclooctatetraene (**3**).

Reduction of the diazocine **1** with zinc and barium hydroxide affords a dihydro derivative which has two readily replaceable (by deuterium exchange) hydrogens and a two-proton olefinic singlet at δ 6.50. Treatment of this dihydro derivative with methyl iodide in the presence of sodium bicarbonate affords a mixture of the monomethyl and dimethyl derivatives **8** and **9**.

The ultraviolet spectra of **1**, **2**, **5**, **8**, and **9** are shown in Figure 1.

A comparison of the ultraviolet spectra of the nonplanar diazocine derivative **1** and the tetrahydro deriva-

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(1) (a) W. W. Paudler and A. G. Zeiler, *Chem. Commun.*, 1077 (1967); (b) *J. Org. Chem.*, **34**, 2138 (1969).

(2) T. J. Katz, M. Yoshida, and L. C. Siew, *J. Amer. Chem. Soc.*, **87**, 4516 (1965).

(3) H. Duval, *Bull. Soc. Chim. Fr.*, **7**, 727 (1910).

(4) J. R. Geigy, British Patent 940165; *Chem. Abstr.*, **61**, 1816 (1964).

(5) The ultraviolet spectrum of the dihydro derivative **6** has recently been compared with that of the *cis*- and *trans*-azobenzene, and it was concluded that compound **6** exists in the indicated tub form [F. Gerson, E. Heilbronner, A. VanVeen, and B. M. Wepster, *Helv. Chim. Acta*, **43**, 1889 (1960)].