When copper nitrate–acetic anhydride was used as the nitration medium, *s*-triazolo[3,4-*a*]phthalazine (1.0 g, 0.006 mol) in acetic anhydride (75 ml), after treatment with a stirred suspension of copper nitrate (1.6 g) in acetic anhydride (20 ml) over 72 hr, gave 3-acetyl-*s*-triazolo[3,4-*a*]phthalazine following dilution of the reaction mixture with water and extraction of the product with chloroform. It was recrystallized from water forming colorless, irregular prisms: 0.10 g (10%); mp 269°; ir (KBr) 3050, 1750, 1630, 1590, 1470, 1300, 1240, 1120, 780, 650 cm^{-1}; nmr ($CDCl_3$) δ 2.82 (s, 3, $COCH_3$), 7.81 (m, 4, aromatic), 8.39 (d, 1, J = 1.5 Hz, H_6).

Anal. Calcd for $C_{11}H_8N_4O \cdot H_2O$: C, 57.48; H, 3.50; N, 24.30. Found: C, 57.45; H, 3.43; N, 23.99.

Registry No.—**2** (R^1 = H; R^2 = Cl), 21517-16-8; **2** (R^1 = H; R^2 = $NHNH_2$), 21517-17-9; **2** (R^1 = H; R^2 = NHN=CHOEt), 21537-96-2; **2** (R^1 = H; R^2 = NHNHCHO), 21517-21-5; **2** (R^1 = $NHNH_2$; R^2 = H), 21517-30-6; **2** (R^1 = R^2 = H) (HBr), 21517-38-4; **4** (R^1 = R^2 = H), 21517-18-0; **4** (R^1 = R^2 = NH_2), 21517-19-1; **5**, 21517-20-4; **6** (R^1 = H; R^2 = NH_2), 21517-22-6; **6** (R^1 = H; R^2 = NH_2) (HBr), 21517-23-7; **7**, 21517-24-8; **9** (R^1 = R^2 = H), 21537-97-3; **9** (R^1 = H; R^2 = CH_3), 21517-26-0; **9** (R^1 = R^2 = CH_3), 21517-27-1; **10**, 21517-28-2; **11**, 12376-93-1; **12**, 21517-34-0; **13** (R = H) (iodide), 21517-31-7; **13** (R = SMe) (methosulfate), 21517-35-1; **14**, 21517-33-9; **15** (R^1 = Me; R^2 = H), 21517-39-5; **15** (R^1 = R^2 = H), 21517-40-8; acyloin of 3-formyl-*s*-triazolo-[3,4-*a*]phthalazine, 21517-36-2; 1-methyl-1-(1-phthalazinyl)hydrazine, 21517-14-6; 2-(1-phthalazinyl)dichloroacethydrazide, 21517-15-7; 3-amino-6-(2-cyanophenyl)-5H-*s*-triazolo[5,1-*c*]-*s*-triazole, 21517-25-9; 3-methyl-5-(2-cyanophenyl)-*s*-triazole, 20062-39-9; 2,3-dimethyl-*s*-triazolo[3,4-*a*]phthalazinium iodide, 21517-32-8; 1,3-dimethyl-*s*-triazolo[3,4-*a*]phthalazinium iodide, 21517-37-3.

Acknowledgments.—The award of a grant from the National Science Foundation (NSF GP 6905) for the purchase of the mass spectrometer used in this study is gratefully acknowledged.

Oxidations with Lead Tetraacetate. III. Cyclization of Ketosemicarbazones to 2-Imino-Δ^3-1,3,4-oxadiazolines[1]

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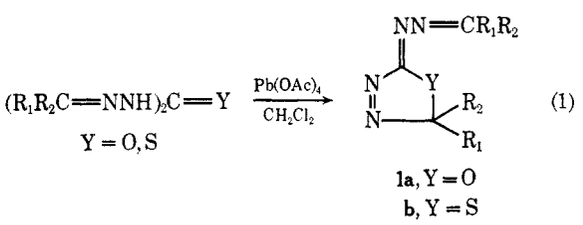
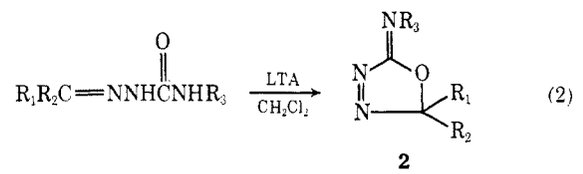
Acetone 4-benzylsemicarbazone is oxidized by lead tetraacetate (LTA) to 5,5-dimethyl-2-benzylimino-Δ^3-1,3,4-oxadiazoline. Eight other members of this new type of oxadiazoline were synthesized. Assignment of the gross structure is based on the spectra of the compounds and on their reactions. The geometry at the exocyclic imino function is not rigorously established but the *anti* (azo) configuration is suggested on the basis of some of the nmr spectra.

Oxidative cyclization of ketocarbohydrazones to oxadiazolines and of acetone thiocarbohydrazone to a thiadiazoline, according to eq 1, were reported recently.[2] We have explored the generality of that type of oxidative ring closure and we now report the synthesis and some properties of related oxadiazolines, eq 2, from semicarbazones and LTA.



(1)

1a, Y = O
b, Y = S

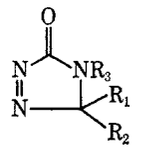


(2)

2

Results and Discussion

The oxadiazoline structure is assigned to the products on the basis of analytical data, molecular weights, spectra, and chemical behavior. The spectra of structures **1** were discussed in detail earlier in establishing those assignments, and the choice of the oxadiazoline structure (**2**) instead of the triazolinone structure (**3**), in the present case, is based largely on analogy.[2]



3

The infrared spectra (Table I) are characterized by a sharp, intense absorption in the region of 1694–1715 cm^{-1}, which can be assigned to the stretching frequency of the exocyclic C=N function.[2] Of the other absorptions noted in Table I, a band in the region of 1114–1156 cm^{-1} appears to be a common feature, regardless of the substituents. It may be caused by a ring vibration associated with the C—O—C function.

The compounds are characterized by two bands in the ultraviolet spectrum, with maxima ranging from 220 to 260 mμ and from 316 to 357 mμ. Both bands must arise from $\pi \rightarrow \pi^*$ transitions.[3] The band at longer wavelength shows fine structure with hydrocarbon solvents and it tails into the visible to obscure the expected weak, $n \rightarrow \pi^*$ (azo) absorption.[3]

(1) Taken, in part, from the Ph.D. Thesis of P. R. West, McMaster University, 1967.

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

(3) An exception is **4** in which R_3 is alkyl. Its $\pi \rightarrow \pi^*$ transition occurs at about 260 mμ and the weaker band at higher wavelength (329 mμ) is probably the $n \rightarrow \pi^*$ band. A shoulder on the high wavelength, $\pi \rightarrow \pi^*$ band in some of the spectra may be caused by an $n \rightarrow \pi^*$ transition.

TABLE I
SPECTRA OF OXADIAZOLINES (2)

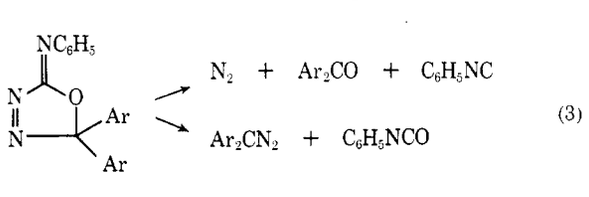
Compd no.	R_1	R_2	R_3	Ir, cm^{-1} [a] C=N stretch	Ir, cm^{-1} [a] Other strong bands i	Ir, cm^{-1} [a] Other strong bands ii	Uv,[b] λ_{max}, mμ (log ϵ_{max})	Pmr, δ[c] R_1, R_2	Pmr, δ[c] R_3
4	Me	Me	$CH_2C_6H_5$	1715	1134	986	260 (3.61)	1.54 s (6 H)	4.56 s (2 H)
						943	329 (2.49)		7.40 m (5 H)
5	Me	Me	C_6H_5	1699	1116	981	221 (3.90)	1.71 s (6 H)	7.2–7.8 m (5 H)
						952	322 (3.82)		
6	Me	Me	*p*-$MeOC_6H_4$	1694	1114	947	231 (4.16)	1.71 s (6 H)	3.95 s (3 H)
						835	357 (4.06)		7.49 q (4 H)
7	Me	Me	*p*-$CH_3C_6H_4$	1697	1115	947	226 (4.00)	1.67 s (6 H)[a]	2.43 s (3 H)[a]
						821	332 (3.89)		7.44 m (4 H)
8	Me	Me	*p*-ClC_6H_4	1701	1115	948	227 (4.02)	1.73 s (6 H)	7.62 s (4 H)
						826	325 (3.82)		
9	C_6H_5	C_6H_5	C_6H_5	1706	1156	1021	220[d] (4.14)	7.0–7.5 m (R_1, R_2, and R_3)	
					1043	901	326 (357 sh) (3.79)		
10	*p*-$CH_3C_6H_4$	*p*-$CH_3C_6H_4$	C_6H_5	1698	1151	1016	224[d] (4.30)	2.32 s (6 H)	
					1037	917	325 (360 sh) (3.82)	6.9–7.8 m (13 H; R_1, R_2, and R_3)	
11	*p*-ClC_6H_4	*p*-ClC_6H_4	C_6H_5	1701	1136	1017	226[d] (4.54)	7.0–7.4 m (R_1, R_2, and R_3)	
					1047	909	329 (357 sh) (3.85)		
12	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	C_6H_5	1701	1152	1008	230[d] (4.38)	3.78 s (6 H)	
					1029	916	324 (357 sh) (3.81)	7.10 q and 7.34 m (13 H); includes R_3	

[a] Carbon tetrachloride solutions. [b] Ethanol (95%) solutions, unless otherwise indicated. [c] Deuteriochloroform solvent, with internal tetramethylsilane (TMS). [d] In hexane.

The nmr spectra of the compounds are in close agreement with those of known oxadiazolines (**1**, Y = O), in those cases where a comparison can be made. Ring methyls of **2** have chemical shifts between δ 1.54 and 1.73, and the shifts caused by changing R_3 from aryl to benzyl to β-phenylethyl[4] is more easily accounted for in terms of *anti* (azo) geometry at the exocyclic nitrogen.

Mass spectra of the products, when run at 70 eV, are devoid of peaks due to masses exceeding M − 56, but 11-eV spectra show the molecular ion and a peak corresponding to M − 28, at least in the case of **4** and **5**. The ready formation of an M − 56 fragment from the oxadiazolines can be rationalized in terms of loss of N_2 and CO.[2]

Chemical reactions of **2** appear to parallel those of **1a**.[2] Catalytic hydrogenation gave back the appropriate parent semicarbazone in good yield, for the compound that was tested (see Experimental Section) and, like their relatives **1a**, compounds **2** are readily destroyed in acidic media. Of particular interest are the products of thermal decomposition of **2**. Kinetic and product studies have shown that two primary pathways compete in the thermolyses of **2** ($R_1 = R_2 =$ Ar; $R_3 = C_6H_5$) as shown in eq 3.[5] The observed



(3)

products (eq 3) are readily accommodated without invoking rearrangements and may be taken as additional support for the oxadiazoline structure.

(4) The chemical shift of ring methyls is δ 1.43 in the β-phenylethyl system: A. M. Cameron, unpublished results.

(5) P. R. West and J. Warkentin, *J. Org. Chem.* **34**, 3233 (1969).

Experimental Section

General.—Ultraviolet and infrared spectra were obtained with a Cary Model 14 and with a Perkin-Elmer 521 instrument, respectively. The nmr spectra were recorded with a Varian A-60 spectrometer with tetramethylsilane as internal reference. Molecular weights were estimated with a Mechrolab Model 301A vapor pressure osmometer, using solutions of the compounds in chloroform. Melting points (uncorrected) were determined with a Thomas "Unimelt," capillary melting point apparatus. In those cases where decomposition occurred, heating was rapid (10°/min^{-1}) to within a few degrees of the melting point. Analyses were by Alfred Bernhardt, Mülheim, Germany, by C. Daessle, Montreal, Canada, and by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Chemicals.—Methylene chloride was used as supplied by Matheson Coleman and Bell (MCB). Lead tetraacetate (MCB), wet with acetic acid, was washed with petroleum ether (bp 30–60°) before use. Semicarbazide hydrochloride was Certified Reagent Grade from Fisher. Commercially available anilines were distilled or recrystallized before use. Benzophenone and *p,p'*-dimethylbenzophenone were Eastman Reagent chemicals and were used as supplied.

Ketones.—*p,p'*-Dichlorobenzophenone was prepared by hydrolysis of the product of the Friedel–Crafts reaction between chlorobenzene and carbon tetrachloride.[6] The crude material contained 2,4'-dichlorobenzophenone, which was partly removed by extraction with low-boiling petroleum ether, in which it is more soluble than the 4,4' isomer. Recrystallization of the residue from aqueous ethanol gave material melting at 145° (lit.[6] mp 145°).

p,p'-Dimethoxybenzophenone, obtained by a slight modification of Unger's procedure,[7] had mp 140–142° (lit.[8] mp 144°).

Semicarbazones.—Unsubstituted semicarbazones were prepared from ketones and semicarbazide hydrochloride according to a standard procedure.[9] A 4-substituted semicarbazone was obtained either by reaction of the appropriate ketone with 4-substituted semicarbazide hydrochloride or by Borsche's method.[10]

(6) J. F. Norris and W. C. Twieg, *Am. Chem. J.*, **30**, 392 (1903).

(7) F. Unger, *Justus Liebigs Ann. Chem.*, **504**, 267 (1933).

(8) R. Quelet and J. Allard, *Bull. Soc. Chim. Fr.*, **7**, 215 (1940).

(9) N. D. Cheronis and J. B. Entriken, "Semimicro Qualitative Organic Analysis," Interscience Publishers, Inc., New York, N. Y., 1957.

(10) W. Borsche, *Chem. Ber.*, **38**, 831 (1905). The semicarbazone is transaminated according to the equation $R_2C{=}NNHCONH_2 + R'NH_2 \rightarrow R_2C{=}NNHCONHR' + NH_3$.

TABLE II

Oxadiazoline[a]	Mp, °C	Purification[b]	Anal., % Calcd C	H	N	Cl	Found C	H	N	Cl	Yield, %
4 ($C_{11}H_{13}N_3O$)[c]	38–39	p	65.00	6.45	20.68		65.14	6.28	20.54		25
5 ($C_{10}H_{11}N_3O$)[d]	72–73	p–c	63.47	5.68	22.21		63.69	5.82	22.20		95
6 ($C_{11}H_{13}N_3O_2$)	94–95	p–c	60.24	5.98	19.18		60.17	5.99	18.74		67
7 ($C_{11}H_{13}N_3O$)	97–98.5	p–c	64.99	6.45	20.69		64.72	6.52	20.42		95
8 ($C_{10}H_{10}N_3OCl$)	85–85.3	e	53.70	4.51	18.79		53.73	4.45	18.53		78
9 ($C_{20}H_{15}N_3O$)	125–128 dec	p–c	76.66	4.83	13.41		76.60	5.11	13.40		20
10 ($C_{22}H_{19}N_3O$)	103–105 dec	p–c	77.39	5.61	12.31		77.46	5.57	12.52		49
11 ($C_{20}H_{13}N_3OCl_2$)	105–110 dec	f, p	62.85	3.40		18.59	63.01	3.37		18.72	20
12 ($C_{22}H_{19}N_3O_3$)	91–93 dec	p	70.76	5.13	11.25		70.97	5.04	11.08		14.5

[a] The oxadiazolines are yellow, except for **4**, which is colorless. [b] Recrystallization solvents: p, petroluem ether; c, chloroform; e, ethanol. Chromatography on Florisil, with petroleum ether as eluent, is indicated by f. [c] Mol wt 203 (calcd), 204 (found). [d] Mol wt 189 (calcd), 183 (found).

Acetone 4-Benzylsemicarbazone.—Acetone semicarbazone (20 g, 0.17 mol), added all at once to stirred, refluxing benzylamine (37.2 g, 0.35 mol), gave (from ethanol) 13.3 g (32%) of N,N'-dibenzylurea, mp 166–167° (lit.[11] mp 167°), and, upon concentration of the filtrate, 6.0 g (17%) of the 4-benzylsemicarbazone, mp 111–112° (lit.[11] mp 113°).

Acetone 4-Phenylsemicarbazone.—Borsche's method[10] gave, from 20 g of acetone semicarbazone and 100 ml of aniline, 10.0 g (30%) of acetone 4-phenylsemicarbazone, mp 154–155.5°, (from ethanol) (lit.[10] mp 155–156°).

Acetone 4-(*p*-Methoxyphenyl)semicarbazone.—Acetone semicarbazone (25.0 g, 0.22 mol) was heated at 160° with *p*-anisidine (40.0 g, 0.33 mol) in 175 ml of bis(2-methoxyethyl) ether. When evolution of ammonia had ceased (15 min) the brown solution was poured into 600 ml of 10% acetic acid, and the precipitate was recrystallized from ethanol. The yield was 11.6 g (24%) and the product melted at 167–169°.

Anal. Calcd for $C_{11}H_{15}N_3O_2$: C, 59.71; H, 6.83; N, 18.99. Found: C, 59.66; H, 6.65; N, 18.75.

Acetone 4-(*p*-Tolyl)semicarbazone.—Acetone semicarbazone (28.8 g, 0.25 mol) was heated at 143° for 30 min with *p*-toluidine (32.2 g, 0.30 mol) in 300 ml of bis(2-methoxyethyl) ether. After the orange-brown solution had cooled, it was poured into 400 ml of 10% acetic acid solution. Filtration of the solid and recrystallization from ethanol–water gave 11.7 g (23%) of the title compound as light tan crystals, mp 174–175° (lit.[12] mp 174–175°).

Acetone 4-(*p*-Chlorophenyl)semicarbazone.—Acetone semicarbazone (28.8 g, 0.25 mol) was heated at 160°, in 150 ml of bis(2-methoxyethyl) ether, with *p*-chloroaniline (38.3 g, 0.30 mol) until evolution of ammonia had ceased. Work-up in the manner described above gave 7.7 g (14%) of the desired product, mp 169–170°.

Anal. Calcd for $C_{10}H_{12}ClN_3O$: C, 53.22; H, 5.36; Cl, 15.71; N, 18.62. Found: C, 53.13; H, 5.65; Cl, 15.62; Cl, 15.62; N, 18.56.

Benzophenone 4-Phenylsemicarbazone.—To a solution of benzophenone (20.0 g, 0.11 mol) in 300 ml of ethanol was added a solution of 4-phenylsemicarbazide hydrochloride[13] (20.6 g, 0.11 mol) and sodium acetate (16.0 g, 0.20 mol) in 50 ml of water. During reflux for 12 hr, the solution became yellow and a fine, white precipitate was formed. The hot solution was filtered and cooled to obtain 7.0 g of white needles. Heating the filtrate 12 hr longer gave, on cooling, a further crop (5.5 g) of benzophenone 4-phenylsemicarbazone (total, 36%). Material so obtained was contaminated with benzophenone azine, which was difficult to remove. Several recrystallizations from ethanol–water gave material melting at 161–163° (lit.[13] mp 163°). Solutions of this material in either ethanol or methylene chloride were pale yellow, however, indicating that traces of ketazine remained.

***p,p'*-Dimethylbenzophenone 4-Phenylsemicarbazone.**—Crude *p,p'*-dimethylbenzophenone semicarbazone (22.3 g, 0.083 mol), mp 135–140° (lit.[14] mp 143–144°), treated with 125 ml of refluxing aniline gave, after two recrystallizations from ethanol–water, 24.9 g of *p,p'*-dimethylbenzophenone 4-phenylsemicarbazone, mp 175–178°. A further recrystallization gave material with mp 178–179°; ir (CCl_4) 3413 (NH) and 1689 (C=O) cm^{-1}; nmr (CCl_4) δ 2.30 and 2.35 (s, 6, CH_3), 7.17 (m, 13, aromatic), NH absorption not seen.

Anal. Calcd for $C_{22}H_{21}N_3O$: C, 76.94; H, 6.16; N, 12.24. Found: C, 77.01; H, 6.23; N, 12.16.

***p,p'*-Dichlorobenzophenone 4-Phenylsemicarbazone.**—From 25.0 g (0.098 mol) of dichlorobenzophenone was obtained 29.5 g (93%) of unsubstituted semicarbazone, mp 190–192° (lit.[14] mp 191.5–192.5°). The product, refluxed with 150 ml of aniline, gave 34.0 g (98.4%) of yellow-brown, ethanol-insoluble crystals. Recrystallization from 300 ml of chloroform gave colorless, rhombic crystals, mp 230–231° (73.5% recovery).

Anal. Calcd for $C_{20}H_{15}Cl_2N_3O$: C, 62.50; H, 3.94; Cl, 18.45; N, 10.93. Found: C, 62.32; H, 3.90; Cl, 18.66; N, 10.83.

***p,p'*-Dimethoxybenzophenone 4-Phenylsemicarbazone.**—Dimethoxybenzophenone formed a semicarbazone very slowly. Treatment of 25.5 g of the ketone with 2 equiv each of semicarbazide hydrochloride and sodium acetate in 300 ml of refluxing, 80% ethanol for 48 hr gave, upon dilution with water, a red oil. The oil was dissolved in chloroform and the solution was washed with water and dried. Evaporation of the chloroform left 23 g of red oil which would not crystallize. Strong infrared bands at 3356 and 1681 cm^{-1} indicated that the desired product was present in high concentration. The oil was, therefore, subjected to the transamination procedure with aniline. Recrystallization of the crude product from chloroform–petroleum ether gave 16.3 g (41% based on ketone) of *p,p'*-dimethoxybenzophenone 4-phenylsemicarbazone as white needles: mp 195–195.5°; ir ($CHCl_3$) 3367 (NH) and 1681 (CO) cm^{-1}; nmr ($CDCl_3$) δ 3.74 and 3.80 (s, 6, CH_3O), 7.25 (m, 13. aromatic).

Anal. Calcd for $C_{22}H_{21}N_3O_3$: C, 70.38; H, 5.64; N, 11.19. Found: C, 70.16; H, 5.14; N, 11.59.

Oxidation of Ketosemicarbazones.—The general procedure involved gradual addition of a semicarbazone in methylene chloride solution to a stirring solution of LTA in methylene chloride. Semicarbazones of dialkyl ketones were oxidized at about 0° (ice cooling) while those of diaryl ketones were oxidized at 30°. The volume of solvent for the semicarbazone was determined in part by its solubility. For benzophenone 4-phenylsemicarbazone the volume of methylene chloride was 10 ml/g, but twice that ratio was required to dissolve the corresponding *p,p'*-dichloro compound. The solvent/oxidant ratio was kept between 5 and 25 ml/g. The more dilute reaction mixtures were usually left for longer times. Yields are probably not optimum and the effects of changing reaction times and concentrations of reagents were not examined. Two syntheses are described below to illustrate procedures. Experimental data for all of the oxidations are tabulated in Table II.

5,5-Dimethyl-2-benzylimino-Δ^3-1,3,4-oxadiazoline (4).—To an ice-cold, stirring solution of LTA (20.0 g, 0.045 mol) in 150 ml of methylene chloride was added, by drops during 1 hr, a solution of acetone 4-benzylsemicarbazone (6.0 g, 0.029 mol) in 60 ml of the same solvent. The mixture was allowed to warm gradually to room temperature during another hour after which time cold water (100 ml) was added. Filtration through a bed of Celite, separation of the organic layer, washing with cold water and with cold bicarbonate solution, drying with Na_2SO_4, evaporation of the solvent with a rotary evaporator, and crystallization of the residue from petroleum ether (bp 30–60°) gave 1.5 g (25%) of

(11) F. J. Wilson, I. V. Hopper, and A. B. Crawford, *J. Chem. Soc.*, **121**, 868 (1922).

(12) P. P. T. Sah and H.-H. Lei, *J. Chin. Chem. Soc.* (Taipei), **2**, 167 (1934); *Chem. Abstr.*, **29**, 465 (1953).

(13) W. Borsche and C. Merkwitz, *Chem. Ber.*, **37**, 3177 (1904).

(14) D. E. Pearson, K. N. Carter, and C. M. Greer, *J. Amer. Chem. Soc.*, **75**, 5905 (1953).

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.

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

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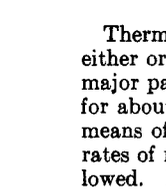
Thermolysis of 5,5-diaryl-2-phenylimino-Δ^3-1,3,4-oxadiazolines (**2a–2d**) at 104.4° in chlorobenzene may take either or both of two pathways, A and B. Path A, leading to N_2, diaryl ketone, and phenyl isocyanide is the major pathway in thermolysis of **2a**. Path B, leading to diaryldiazomethane and 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,



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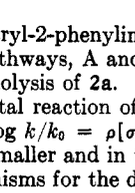
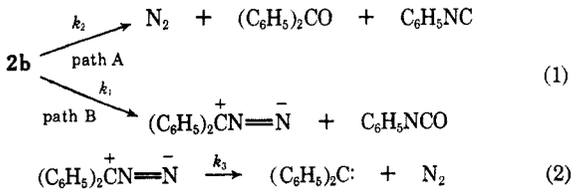
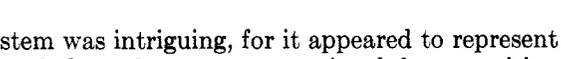


2a, $R_1 = R_2 = p\text{-}C_6H_4Cl$; $R_3 = C_6H_5$
b, $R_1 = R_2 = R_3 = C_6H_5$
c, $R_1 = R_2 = p\text{-}C_6H_4CH_3$; $R_3 = C_6H_5$
d, $R_1 = R_2 = p\text{-}C_6H_4OCH_3$; $R_3 = C_6H_5$

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



(1)



(2)

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

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