

TABLE II
 AMIDES FROM BIFURANDIONE

	Reactant	Solvent	Reaction temp., °C.	Product	Yield, %	M.p., °C.	Analyses							
							Calculated			Mol. wt.	Found			Mol. wt.
							C	H	N		C	H	N	
1	<i>n</i> -C ₄ H ₉ NH ₂	Dioxane, methanol or none	Room	XVI	75	166	60.75	6.37	5.90	237	60.65	6.38	5.96	230
											60.55	6.18	5.96	245
2	<i>i</i> -C ₄ H ₉ NH ₂	Dioxane	Room	XVI	57	175 d.	60.75	6.37	5.90		61.24	6.43	5.92	
3	(CH ₃) ₂ NH	Water	Room	XVII	28	200-220 d.	57.41	5.30	6.70	209	57.54	5.20	6.74	235
												6.63	235	
4	<i>n</i> -Octadecyl amine	Dioxane	100	XVI	20	135-140	72.01	10.00	3.23		71.95	10.19	3.39	
											71.55	10.13	3.35	
											71.49	10.18		
5	<i>p</i> -Toluidine	Dioxane	100	XVIII	49	244-252 d.	66.41	4.83	5.16		66.23	4.89	5.31	
6	<i>p</i> -Aminobenzoic acid	Acetic acid	110	XVIII	94	258-263	59.80	3.68	4.65		59.10	3.95	4.70	
												4.41		
7	Dodecylaniline (mixt. of isomers)	Dioxane	100	XVIII	1	199-201	73.38	8.29	3.29		73.13	8.35	3.38	
												3.46		

ylformamide, from which a yellow powder (XX, Ar = α -C₁₀H₇), m.p. 298-302°, was obtained by addition of water.

Anal. Calcd. for C₁₈H₂₃O₃N₃: N, 7.30. Found: N, 7.33, 7.38.

Reaction of I with *p*-Nitrophenyl Radicals.—A sample of bifurandione (8.2 g., 0.050 mole) was almost completely dissolved in 800 ml. of acetone by warming on a steam-bath. After addition of 1 g. of cupric chloride dihydrate, the solution was removed from the steam-bath and a slurry of 12 g. (0.051 mole) of *p*-nitrobenzenediazonium fluoborate⁷ in 120 ml. of water was slowly added with stirring. The mixture, which was at about room temperature by the time addition was complete, was warmed on the steam-bath for another two hours; then 5.8 g. of a reddish-brown precipitate was collected by filtration. Some unchanged bifurandione was removed by extraction with hot methyl ethyl ketone from the sparingly soluble *p*-nitrophenyl- $\Delta^{2,2'}$ (5H,5'H)-bifuran-5,5'-dione (XXI), which was then recrystallized from acetone, m.p. 230-240° dec.; ultraviolet absorption:

(7) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 225.

λ_{\max} 3800 Å., ϵ 47,300; infrared absorption: similar to bifurandione with additional bands at 6.6 and 7.45 ($-\text{NO}_2$ group) and 11.75 μ (*p*-substituted aromatic).

Anal. Calcd. for C₁₄H₇O₃N₃: C, 58.96; H, 2.47; N, 4.91. Found: C, 59.12; H, 2.54; N, 5.48, 5.10.

Chlorination of Bifurandione.—A solution of 23.4 g. of bifurandione in 1800 ml. of acetic acid was chlorinated at 100° for 12 hours. Some hydrogen chloride was evolved during this period. The solution, which turned green, was concentrated under reduced pressure to remove not only the solvent but some chlorinated acetic acids which had formed during the reaction. A gelatinous solid remained. Recrystallization from chloroform gave a brown powder (1.0 g., 3%), m.p. 150-160°. After repeated recrystallizations from ethyl alcohol, white needles of the dichloride were obtained, m.p. 169.5°.

Anal. Calcd. for C₈H₄O₂Cl₂: C, 40.87; H, 1.75; Cl, 30.17. Found: C, 41.09, 41.06; H, 1.90, 1.94; Cl, 29.82, 29.78.

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[CONTRIBUTION NO. 513 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Bifurandione. IV. Polarographic Reduction

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The polarographic reductions of *cis*- and *trans*- $\Delta^{2,2'}$ (5H,5'H)-bifuran-5,5'-dione have been studied as a function of pH in 1:1 acetonitrile-water solutions and also in 50% H₂SO₄ solutions by volume. In acetonitrile-water solutions the half-wave potential of the first wave shifts about 0.060 mv. per pH unit over the range 0 to 5.5. Evidence is presented for stepwise hydrolysis of the two lactone rings of each isomer to give rise to reducible forms having different half-wave potentials from the original isomer. In both acetonitrile-water and 50% sulfuric acid solutions the reduction appears to be a two-electron reduction.

Synthesis of the unusual unsaturated dilactone¹ $\Delta^{2,2'}$ (5H,5'H)-bifuran-5,5'-dione has prompted a polarographic study of its behavior at the dropping mercury electrode. The present work was undertaken to determine whether or not differences would be observed in the polarographic behavior of the *cis* and *trans* isomers and whether or not stepwise hydrolysis of the rings of the two isomers would

lead to different reducible products. In addition, since its structure bears some resemblance to coumarin, it was of interest to compare its polarographic behavior with published information on that of coumarin.²⁻⁵ To this end we have studied the polarographic behavior of the *cis* and *trans*

(2) O. Capka, *Coll. Czech. Chem. Commun.*, **15**, 965 (1950).

(3) A. J. Harle and L. E. Lyons, *J. Chem. Soc.*, 1575 (1950).

(4) R. Patzak and L. Neugebauer, *Monatsh.*, **82**, 662 (1951).

(5) R. Patzak and L. Neugebauer, *ibid.*, **83**, 776 (1952).

(1) J. C. Sauer, R. Cramer, V. A. Engelhardt, T. A. Ford, H. E. Holmquist and B. W. Howk, *This Journal*, **81**, 3677 (1959).

isomers in 1:1 acetonitrile-water solutions over the apparent pH range of 1 to 12. Since the *cis* form can be obtained from the *trans* form by the action of concentrated sulfuric acid, we have also studied the behavior of the two isomers in 50% sulfuric acid by volume. The controlled potential electrolysis of bifurandione was carried out in concentrated sulfuric acid and the product isolated.

Experimental

The polarographic studies were carried out on a Leeds and Northrup Electrochemograph, type E. Half-wave potentials were corrected for IR drop. A conventional H-cell, with an aqueous KNO_3 bridge in one leg connected to an external saturated calomel reference electrode, was used for the runs made in 1:1 acetonitrile-water. The external saturated calomel electrode was a test-tube with a side arm which contained a capillary tip packed with filter paper. For the work in 50% sulfuric acid solutions a single-compartment cell was used in combination with either a similar external saturated calomel electrode or a mercurous sulfate reference electrode. Britton and Robinson buffers were used for the acetonitrile-water studies.

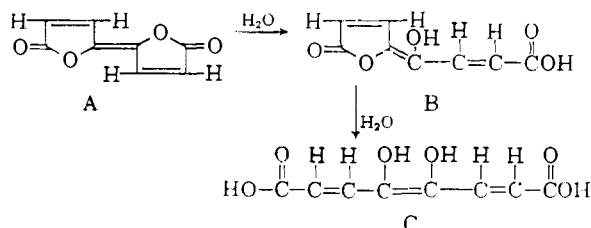
The characteristics of the capillary were: $m = 2.484$ mg./sec. determined in air with a 60-cm. head of mercury, and $t = 3.4$ in 1:1 CH_3CN-H_2O measured in an open circuit. The acetonitrile was Eastman technical grade used without further purification. The Emulphor ON 870 used for maximum suppression in some of the sulfuric acid solutions was obtained from General Aniline and Film Corporation.

The macroelectrolyses were carried out using an Analytical Instruments potentiostat. The ultraviolet spectra were recorded on a Cary model 14 instrument. The pH measurements were made on a Beckman model G pH meter and are apparent values since correction for non-aqueous junction potentials was not made.

Results and Discussion

1:1 Acetonitrile-Water.—Because of the insolubility of bifurandione in water it was necessary to use aqueous-non-aqueous mixtures if the reduction was to be studied as a function of pH . The choice of a 1:1 mixture of acetonitrile-water was somewhat arbitrary, but it provided a mixture capable of dissolving the buffers used and still provided workable solubility for the bifurandione, *i.e.*, 10^{-3} molar solutions of *cis*- and *trans*-bifurandione, the *cis* form being slightly less soluble than the *trans*.

The reduction of the *cis* and *trans* isomers of bifurandione was identical within experimental error over the pH range studied. Over the pH range from 0 to approximately 4, a single well-defined wave is obtained. As the pH is increased, the limiting current for this wave decreases and a second wave develops, the limiting current of which increases to a maximum and then decreases with further increase of pH . At the same time a third wave develops, the height of which increases with further increase of pH . This behavior is interpreted as stepwise hydrolytic cleavage of the rings and may be written in the following manner for the *trans* form



Each of the hydrolysis products is itself reducible, but reduces at somewhat different potentials, form C reducing at more negative potentials than form B. Since the appearance of the second and third reduction waves is also a function of the age of the solution as well as pH , the curves were obtained as soon after preparation as possible, consistent with the problems of transfer to the cell and deaeration. Since forms B and C can exist as *cis* and *trans* isomers as well as acid and anion forms, it was thought that these differences might be detected polarographically, although both B and C forms would probably be in the anion form at the pH values (10.3) involved. Chances for observing reduction waves for these latter two forms would then be less probable than for the *cis* and *trans* forms.

The character of the waves as a function of pH is shown in Fig. 1. Variations of $E_{1/2}$ and limiting

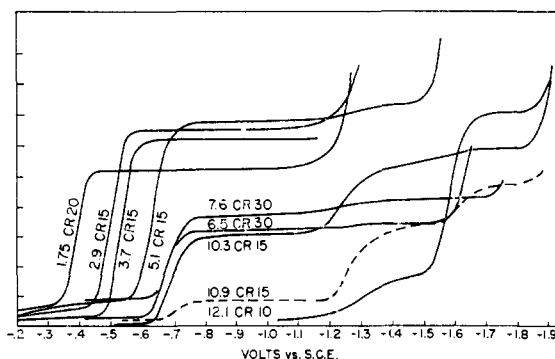


Fig. 1.—Reduction of *trans* bifurandione as a function of pH . CR represents current range and the number following is a factor which if multiplied against the wave height in μ amperes, makes the wave heights comparable.

current for the first wave as a function of pH are presented in Table I for both isomers of bifurandione. Plots of pH vs. $E_{1/2}$ give straight lines with a slope of 0.062 over the pH range of 0 to 5.5. Beyond a pH of 7.5 the reduction becomes pH independent. A curve extrapolated to a pH of 0 gave a value for $E_{1/2}$ of -0.300 volt vs. the S.C.E.

TABLE I
VARIATION OF $E_{1/2}$ AND i_d vs. pH FOR THE FIRST WAVE OF
1.58 mM *trans*- AND 0.96 mM *cis*-BIFURANDIONE

Apparent pH	<i>trans</i>		<i>cis</i>	
	$-E_{1/2}$ corr., v. vs. S.C.E.	i_d , μ amps	$-E_{1/2}$ corr., v. vs. S.C.E.	i_d , μ amps
1.2	0.373	14.92	0.379	9.4
2.9	.487	15.3	.486	9.0
3.7	.525	15.0	.523	8.9
5.1	.615	15.0	.629	8.9
6.5	.666	14.5	.661	9.0
7.6	.678	13.9	.682	8.3
8.7	.677	12.6	.678	7.9
10.3	.682	7.7	.689	4.4
10.9	.687	3.1	.699	1.0
12.1	Disappeared		Disappeared	

The limiting current of the first wave remains fairly constant up to a pH of 4, but begins to decrease with increasing pH at this point. Under the conditions of this experiment the second wave was evident at this point, but was not sufficiently

TABLE II
VARIATION OF $E_{1/2}$ AND i_d vs. pH FOR SECOND AND THIRD WAVES OF 1.58 mM *trans*- AND 0.96 mM *cis*-BIFURANDIONE

Apparent pH	<i>trans</i>			<i>cis</i>				
	(2) $-E_{1/2}$ corr., v. vs. S.C.E.	i_d , μ amps	(3) $-E_{1/2}$ corr., v. vs. S.C.E.	i_d , μ amps	(2) $-E_{1/2}$ corr., v. vs. S.C.E.	i_d , μ amps	(3) $-E_{1/2}$ corr., v. vs. S.C.E.	i_d , μ amps
10.3	1.235	5.3			1.233	3.0		
10.9	1.278	6.3	1.658	1.70	1.270	4.2	1.615	2.0
12.1	1.316	1.7	1.590	9.4	1.290	1.3	1.580	5.4

defined to graphically calculate a half-wave potential or limiting current until a pH of 10.3.

At a pH of 10.9 under these same conditions of minimum age of solutions, the second wave had reached its maximum limiting current and the third wave was in evidence. At this point the first wave had decreased to less than one-fourth its maximum limiting current. At a pH of 12.1 the first wave had disappeared, the second wave had nearly disappeared, and the third wave was well defined with a limiting current of approximately two-thirds that of the maximum wave height for the first wave. These data are presented in Table II.

If the solutions are allowed to age an hour before running the polarograms, the second wave appears as early as pH 4. The data presented in Table III were obtained in earlier work in which a Beckman fiber-type electrode was used as a reference and the half-wave potentials were not corrected for resistance. In addition, the capillary characteristics were not measured, so direct comparison of half-wave potentials and diffusion currents with the values in Tables I and II is not possible.

TABLE III
VARIATION OF HALF-WAVE POTENTIAL AND $i_{d/c}$ FOR 0.65 mM *trans*-BIFURANDIONE SOLUTIONS WHICH HAD AGED FOR AN HOUR BEFORE RUNNING POLAROGRAMS

pH	Uncorr. $-E_{1/2}$ (1), v. vs. S.C.E.	Uncorr. $-E_{1/2}$ (2), v. vs. S.C.E.	Uncorr. $-E_{1/2}$ (3), v. vs. S.C.E.	$i_{d/c}$ (1)	$i_{d/c}$ (2)	$i_{d/c}$ (3)
2.4	-0.54			6.61		
3.9	-.64	-0.99		6.33	0.18	
5.7	-.71	-1.08		6.22	.29	
7.1	-.75	-1.19		5.85	.52	
8.1	-.76	-1.24		4.38	.89	
9.0	-.76	-1.27		3.68	2.34	
10.0		-1.25			3.19	
11.4		-1.28	-1.72		1.34	1.40
12.6			-1.66			4.08

Ultraviolet absorption spectra were obtained as a function of pH for *trans*-bifurandione in 1:1 acetonitrile-water solutions. These data are presented in Table IV and, as can be seen, the absorption maximum shifts toward the visible with increasing pH . At a pH of 10.1 a jump of 140 Å. occurs which is interpreted as hydrolysis of the first ring, the compound existing in the B form. The absorptivity $[a]$ decreases with pH as form A is hydrolyzed. At a pH of 11.5 the absorptivity increases slightly as a maximum amount of B is formed and then decreases again at a pH of 12.6 as B is hydrolyzed to form C.

Because of this interesting behavior with pH , it was felt desirable to study this hydrolysis with

TABLE IV
ULTRAVIOLET BEHAVIOR OF *trans*-BIFURANDIONE AS A FUNCTION OF pH . CONCENTRATION 0.01 G./LITER

pH	λ_{max}	a^a
2.4	3400	222
3.9	3420	215
5.7	3430	212
7.1	3435	174
8.2	3440	161
9.2	3460	117
10.1	3800	118
11.5	3830	159
12.6	3860	127

^a Absorbance divided by concentration in g./l.

time. For this purpose a pH of 10.3 was chosen, since all three waves occur at this pH , and it is thus possible to study the appearance or disappearance of all three entities. Figure 2 shows diagrammatically the appearance and disappearance of the waves with time. These studies were carried out for a period of about forty hours for the *trans* isomer and about twenty hours for the *cis*. At this point, because of the accumulation of mercury in the polarographic cell, it was impossible to deaerate the solution, and the oxygen maximum masked the waves. During the course of this study it was observed that the second wave appears to be made up of two different reductions which have half-wave potentials so close as to be unresolvable. This behavior is illustrated in curves e, f, and g of Fig. 2 and occurs in studies on both the *cis* and *trans* forms and may be due to the *cis* and *trans* isomers of form B. Undissociated acid and anion forms could also cause this effect, but it is considered unlikely that the undissociated acid would exist at this pH . The disappearance of the first wave or hydrolysis of the first ring was found to be a first-order reaction. A plot of time vs. the log of $[a-x]$ in which $[a]$ is the initial concentration and $[x]$ is the change in concentration after time $[t]$ gave a straight line. Calculation of the rate constant $[k]$ from the slope of these lines gave a value of 1.6×10^2 for the *trans* form and 1.7×10^2 for the *cis*.

Concentration studies were carried out with the *trans* isomer in 1:1 acetonitrile-water solutions at a pH of 1.15 and it was found that the Ilkovic equation was followed over the concentration range of 3×10^{-4} to 1.6×10^{-3} molar. Values of I , the diffusion coefficient, or $i_d/cm^{3/4}v^{1/2}$ calculated at a pH of 1.15, were 4.28 and 4.17 for the *trans* and *cis* isomers, respectively. The half-wave potential is invariant with concentration.

Little work has been published on acetonitrile-water mixtures, so a comparison of I values is difficult. Wawzonek, *et al.*, however, presented

data⁶ on 2-methyl-1,4-naphthohydroquinone in an acetonitrile medium containing 42.9% water by volume. Their data give a value for I of 3.32 for a two-electron reduction. Our data would appear to be in reasonable agreement for a two-electron reduction.

Plots of $\log i/i_d - i$ vs. E were made on the first wave of the *trans* and *cis* reductions in buffered solutions. The values for the reciprocal of the slope and the values of α , defined as 0.059 divided by the reciprocal of the slope, are given in Table V. At the most acid values of pH , α is close to two, indicative of a two-electron reversible reduction. Calculation of a diffusion constant, assuming $n = 2$, gives a value of 1.23×10^{-6} cm./sec. for both forms.

TABLE V

VALUES OF SLOPE AND α OBTAINED FROM PLOTS OF $\log i/i_d - i$ vs. E FOR THE FIRST WAVE OF *cis*- AND *trans*-BIFURANDIONE IN BUFFERED SOLUTIONS

pH	<i>trans</i>		<i>cis</i>	
	Reciprocal of slope	α	Reciprocal of slope	α
1.2	0.026	2.3	0.030	2.0
2.9	.037	1.6	.039	1.5
3.7	.032	1.8	.034	1.7
5.1	.045	1.3	.038	1.6
6.5	.041	1.4	.040	1.5
7.5	.048	1.2	.042	1.4
8.7	.053	1.1	.051	1.2

Attempts were made to carry out controlled potential electrolyses with subsequent isolation of the reduction product. Because of the low solubility of the bifurandione in this medium and the solubility of the reduction product, all efforts to isolate a product failed.

The behavior of bifurandione is similar in some respects to that published on coumarin^{3,4} with three notable exceptions. The half-wave potential is dependent on pH in the acid region in contrast to the behavior reported for coumarin. Capka,² however, does report a pH dependency of half-wave potential for coumarin in the pH range 4.8 to 7.5. Another exception is that the acid forms of bifurandione are reducible in contrast to coumarin. The marked change in absorption occurs at about the same pH for bifurandione as for coumarin. The final exception is that while coumarin appears to be a one-electron reduction, bifurandione appears to undergo a two-electron reduction.

Sulfuric Acid Behavior.—Since bifurandione is most soluble in concentrated sulfuric acid, controlled potential studies were carried out in this medium in an effort to isolate a product. These electrolyses were run using a mercury pool cathode and a mercurous sulfate reference electrode. The electrolysis was carried out at a potential of -0.80 volt. A product was crystallized out by pouring

(6) S. Wawzonek, R. Berkey, E. W. Blaha and M. E. Runner, *J. Electrochem. Soc.*, **103**, 456 (1956).

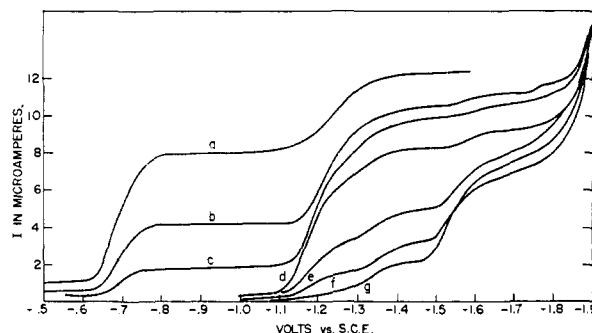
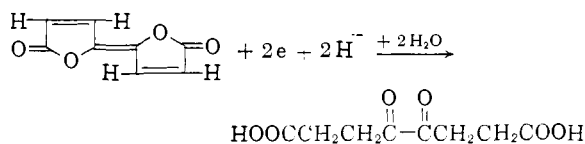


Fig. 2.—Reduction of 6.42 mM of *trans*-bifurandione at a pH of 10.3 as a function of time: a, 7 minutes; b, 27 minutes; c, 54 minutes; d, 364 minutes; e, 1036 minutes; f, 1169 minutes; g, 2551 minutes.

the cell contents, after electrolysis, into ice-water. The product was subsequently identified as 4,5-dioxooctanedioic acid.^{7,8}

The reduction process can be considered as a two-electron hydrogenation or a 1,6-addition to the conjugated double bond system of 4,5-dihydroxy-2,4,6-octatriendioic acid. Whether the ring undergoes acid hydrolysis prior to reduction or after addition of the electrons cannot be determined from the data available, nor can it be determined whether the same reduction mechanism is in effect in the acetonitrile-water medium. The over-all reduction can be represented as



Because of the success of the controlled potential work in sulfuric acid medium, it was of interest to observe the polarographic behavior in the same medium. The presence of maxima in concentrated sulfuric acid and the non-reproducibility of the behavior with time led to use of 50% sulfuric acid solutions by volume. A single wave which contained a slight maximum was obtained in 50% H_2SO_4 medium. The maximum was suppressed by 0.3 ml. of 0.5% by weight Emulphor ON in 10 ml. of solution. The half-wave potential was invariant with concentration and was -0.28 volt vs. the S.C.E. for the *trans* isomer, and -0.26 volt vs. the S.C.E. for the *cis*. The isomers obeyed the Ilkovic equation, a value of 1.54 being obtained for $i_d/cm^2/t^{1/2}$. Plots of $i/(i_d - i)$ vs. E for the *cis* and *trans* isomers gave reciprocal slope values of 0.0295 for both, indicating a two-electron reversible reduction in agreement with the controlled potential reduction.

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(7) I am indebted to Miss Lucille Williams for carrying out the controlled potential work.

(8) H. E. Holmquist, J. C. Sauer, V. A. Engelhardt and B. W. Howk, *THIS JOURNAL*, **81**, 3686 (1959).