80. F. A. Burker, R. E. Busby, M. Iqbal, J. Parrick, and C. J. Shaw, Chem. Ind., No. 38, 1344 (1969).
81. H. L. Reice and T. E. Londergan, J. Am. Chem. Soc., 77, 2678 (1955).
82. R. Nicoletti and M. R. Forsellese, Gazz. Chim. Ital., 95, 83 (1965).
83. R. C. Blume and H. J. Lindwall, J. Org. Chem., 10, 255 (1945).
84. R. Boid and C. Rodsen, Biochem. J., 29, 555 (1935).
85. R. E. Busby, S. M. Hussan, J. Iqbal, M. A. Khar, J. Parrick, and C. J. Shaw, J. Chem. Soc., Perkin Trans. I, No. 11, 2782 (1979).
86. R. L. Jones and C. W. Reese, J. Chem. Soc., C, No. 17, 2249 (1969).
87. A. Gambacorta, R. Nicoletti, and M. L. Forsellese, Tetrahedron, 27, 985 (1971).
88. W. Kirmse, in: Carbene Chemistry, Academic Press, New York (1971), p. 398.
89. B. Robinson, Tetrahedron Lett., No. 2, 139 (1962).
90. C. W. Reese and C. E. Smithen, J. Chem. Soc., No. 8, 938 (1964).
91. H. E. Dobbs, Tetrahedron, 24, 491 (1968).
92. G. Elinger, Chem. Ber., 39, 2115 (1906).
93. K. Auwers and F. Winternitz, Chem. Ber., 35, 465 (1902).
94. R. E. Busby, M. Iqbal, J. Parrick, and C. J. Shaw, Chem. Commun., No. 22, 1344 (1969).
95. R. L. Jones and C. W. Reese, J. Chem. Soc., No. 17, 2251 (1969).
96. R. E. Busby, J. Parrick, M. H. Rizvi, and C. J. G. Shaw, J. Chem. Soc., Perkin Trans. I, No. 11, 2786 (1979).
97. R. Daniels and L. Salerni, Proc. Chem. Soc., No. 1, 286 (1960).
98. V. Marolt, B. Stanovnik, M. Tišler, and B. Vercek, Vesth. Slov. Hem. Drast., 25, 265 (1978).
99. J. Zugrarescu, E. Rucinschi, and G. Suprateanu, Tetrahedron Lett., No. 12, 941 (1970).
100. I. A. D'yakonov, T. V. Mandel'shtam, and O. M. Radul, Zh. Org. Khim., 4, 723 (1968).
101. E. E. Sweheizer and G. J. O'Neill, J. Org. Chem., 28, 2460 (1963).
102. J. Maas, G. B. R. de Graf, and H. J. Hertod, Rec. Trav. Chim., 74, 175 (1955).
103. M. P. Cara and N. K. Bhattaacaryyam, J. Org. Chem., 23, 1614 (1958).
104. W. Triebs, H. Barchet, G. Bush, and W. Kirchoff, Lieb. Ann., 574, 54 (1951).
105. H. W. Whitlock and N. A. Carlson, Tetrahedron, 20, 2101 (1964).

KINETICS OF OPENING OF THE RING OF 5-ARYL-2,3-DIHYDROFURAN-2,3-DIONES UNDER THE INFLUENCE OF METHANOL*

Yu. S. Andreichikov, Yu. A. Nalimova,
M. I. Vakhrin, S. P. Tendryakova,
and A. P. Kozlov

UDC 547.724: 542.92 +
541.127

The kinetics of the opening of the ring of 5-aryl-2,3-dihydrofuran-2,3-diones under the influence of methanol, which leads to the formation of methyl esters of aroylpyruvic acids, were studied by PMR spectroscopy. A mechanism is proposed for the reaction.

It is known that the furan ring of 5-aryl-2,3-dihydrofuran-2,3-diones [1] is readily opened under the influence of nucleophilic reagents. Thus lower aliphatic alcohols react with I to give esters of aroylpyruvic acids when the reaction mixtures are heated at 60-70°C for 3 min [2]. The reaction of I with amines, hydrazines, and hydroxylamines is used as a method for the preparation of the corresponding derivatives of aroylpyruvic acids [3].

---

* Communication 26 from the series "Chemistry of oxalyl derivatives of methyl ketones." See [1] for Communication 25.

Perm State Pharmaceutical Institute, Perm 614600. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 744-746, June, 1982. Original article submitted June 11, 1981.

0009-3122/82/1806-0560$07.50

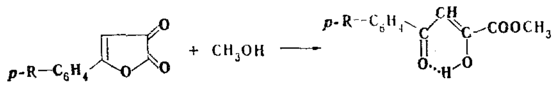
TABLE 1. Rate Constants for the Reaction of 5-Aryl-2,3-dihydrofuran-2,3-diones Ia-e with Methanol in Dioxane

Compound	$k \cdot 10^2$, liters/mole-min		
	18,5°	28°	36,5°
Ia	1,42±0,12	2,15±0,12	3,00±0,23
Ib	1,93±0,12	3,07±0,05	4,08±0,16
Ic	3,82±0,04	7,24±0,14	9,71±0,13
Id	24,65±0,11	39,28±0,17	49,60±0,75
Ie	25,84±0,03	42,60±0,11	64,20±0,12

TABLE 2. Parameters of the log k vs σ Correlation

T, °C	r	ρ	S
18,5	0,990	2,947	0,076
28,1	0,989	2,968	0,080
36,5	0,988	2,982	0,084

To ascertain the mechanism of opening of the furan ring we investigated the kinetics of the reaction of Ia-e with methanol, which leads to the formation of methyl aroylpyruvates II.



Ia-e IIa-e

I, II a R=OCH$_3$; b R=CH$_3$; c R=H; d R=Br; e R=Cl

The kinetics of the reaction were studied by PMR spectroscopy at 18.5-36.5°C in dioxane at Ia-e concentrations of $2.7 \cdot 10^{-2}$ mole/liter and a methanol concentration of $25 \cdot 10^{-2}$ mole/liter. The rate of the reaction was determined by establishing the decrease in the intensity of the signal of the CH group of the starting furandione at 6.75 ppm and the increase in the intensity of the signal of the methylidyne proton of the resulting methyl aroylpyruvates, which are known [4] to exist in the enol form in solutions.

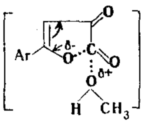
Two centers for nucleophilic attack by the reagent, viz. the carbonyl groups in the 2 and 3 positions of the furan ring, are present in 5-aryl-2,3-dihydrofuran-2,3-diones Ia-e. An analysis of the limiting resonance structures of Ia-e and an estimate of their stabilities and the contributions of the hybrid structures [5] indicate commensurable reactivities of these centers, whereas the ease of ring opening constitutes evidence for the significantly greater reactivity of the carbonyl group in the 2 position.

It was established that the reaction is described by the rate equation for second-order reactions [6]. The second-order rate constants (k) are presented in Table 1.

An analysis of the experimental data made it possible to establish that the logarithms of the rate constants (log k) correlate satisfactorily with the σ and σ^0 substituent constants. The parameters of the log k vs σ correlation are presented in Table 2.

The large absolute ρ and ρ^0 values constitute evidence that significant negative charge develops on the reaction center in direct proximity to substituent R in the transition state of the reaction [7].

The following structure of the transition state, in which negative charge develops on the lactone oxygen atom, can be imagined:



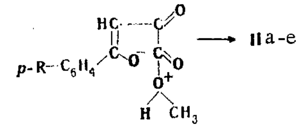
Charge delocalization of the enolate anion type and significant stabilization by electron-acceptor substituents, in agreement with the large positive ρ and ρ^0 values, are possible in this case. This provides a basis for giving preference to this structure or a structure close to it for the transition state.

TABLE 3. Activation Parameters for Opening of the Ring of 5-Aryl-2,3-dihydrofuran-2,3-diones under the Influence of Methanol

Compound	E, kJ/mole	lg A	$\Delta S^{\neq}$, eu	$\Delta G^{\neq}$, kJ/mole 18.5-36.5 deg
Ia	31,1	3,7	−43,5	82,8
Ib	32,9	4,18	−41,4	82,0
Ic	39,0	5,6	−34,9	80,1
Id	29,1	4,6	−39,4	75,7
Ie	37,8	6,2	−32,2	75,5

The negative charge on the reaction center indicates that the formation of a C−O bond between the carbonyl carbon atom and the oxygen atom of the alcoholic hydroxy group somewhat precedes cleavage of the C−O bond between the carbonyl carbon atom and the lactone oxygen atom. The last step of the reaction is also the rate-determining step.

The reaction subsequently proceeds via the scheme



The activation parameters of the reaction are presented in Table 3.

The low values of the energy of activation (E) and the significant negative values of the entropy of activation ($\Delta S^{\neq}$) constitute evidence in favor of the proposed reaction mechanism, which has a number of features in common with a mechanism involving synchronous nucleophilic substitution (S_N2) [7].

EXPERIMENTAL

The reaction rates were determined from the time dependence of the concentrations of the starting compounds and products. The PMR spectra were recorded with an RS-60 spectrometer. The temperature of the samples was maintained at a constant value with an accuracy of ± 0.5°C. The temperature was measured with a methanol NMR thermometer and also by means of a thermocouple. In the latter case the emf of the thermocouple was measured by a compensation method with the aid of an R-307 potentiometer. The accuracy in the determination of the temperature was ± 0.2°C. The concentrations of the substances were determined from the integral intensities of the absorption lines of the CH groups in the spectra; the amplitudes of the signals of the CH groups of the starting compounds and the reaction products were also measured in order to increase the accuracy of the results. Since relaxation times T_2 of the recorded signals were close, the error in the determination of the concentrations of the substances by this method was lower. The rate constants were calculated from the equation for a second-order reaction [6].

LITERATURE CITED

1. Yu. S. Andreichikov, L. F. Gein, and V. L. Gein, Zh. Org. Khim., 17, 631 (1981).
2. Yu. S. Andreichikov, S. P. Tendryakova, Yu. A. Nalimova, and G. D. Plakhina, Khim. Geterotsikl. Soedin., No. 8, 1030 (1977).
3. Yu. S. Andreichikov, Yu. A. Nalimova, S. P. Tendryakova, and Ya. M. Vilenchik, Zh. Org. Khim., 14, 160 (1977).
4. L. N. Kurkovskaya, N. N. Shapet'ko, Yu. S. Andreichikov, and R. F. Saraeva, Zh. Struk. Khim., 13, 1026 (1972).
5. A. S. Dneprovskii and T. I. Temnikova, Theoretical Foundations of Organic Chemistry [in Russian], Khimiya, Leningrad (1979), pp. 48, 224.
6. K. Leidler, Kinetics of Organic Reactions [Russian translation], Mir, Moscow (1966), p. 53.
7. R. W. Hoffmann, Mechanisms of Chemical Reactions [Russian translation], Khimiya, Moscow (1979), pp. 45, 64, 103.