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Synthesis and Reactions of Perylenecarboxylic Acid Derivatives. VII. Hydrolysis of *N,N'*-Dialkyl-3,4 : 9,10-Perylenebis(dicarboximide) with Sulfuric Acid

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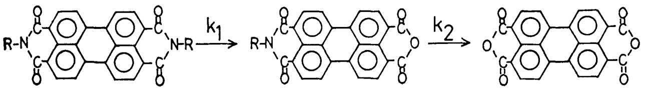
(Received August 6, 1980)

Synopsis. The hydrolysis of *N,N'*-dialkyl-3,4 : 9,10-perylenebis(dicarboximide) (alkyl$=$CH$_3$, CH$_2$CH$_3$, CH$_2$CH$_2$CH$_3$, and CH$_2$CH$_2$CH$_2$CH$_3$) with sulfuric acid at 180—200 °C gave *N*-alkyl-3,4 : 9,10-perylenetetracarboxylic monoanhydride monoimide (alkyl$=$CH$_3$, CH$_2$CH$_3$, CH$_2$CH$_2$CH$_3$, and CH$_2$CH$_2$CH$_2$CH$_3$). The kinetics of the reaction were determined spectroscopically.

Previous work has shown that 3,4 : 9,10-perylenetetracarboxylic monoanhydride monoimide (**2a**—**e**) can be prepared by the condensation of 3,4 : 9,10-perylenetetracarboxylic dianhydride (**3**) with alkylamine.1) The condensation of **2a**—**e** with arylamine gave *N*-alkyl-*N'*-aryl-3,4 : 9,10-perylenebis(dicarboximide).2) This work was undertaken to examine whether **2b**—**e** could be prepared from *N,N'*-dialkyl-3,4 : 9,10-perylenebis(dicarboximide) (**1b**—**e**). **2a** was prepared by the hydrolysis of 3,4 : 9,10-perylenebis(dicarboximide) (**1a**) with sulfuric acid.3) The formation of **2b**—**e** in the hydrolysis of **1b**—**e** with sulfuric acid was then determined.



1a~e 2a~e 3

R = a; H, b; CH$_3$, c; CH$_2$CH$_3$, d; CH$_2$CH$_2$CH$_3$,
e; CH$_2$CH$_2$CH$_2$CH$_3$

Experimental

Materials. **1b**—**e**, **2b**—**e**, and **3** were prepared by the procedures reported before.1)

Hydrolysis. A flask containing 50.0 ml of 95%-sulfuric acid was set in a thermostated bath at the reaction temperature. To the flask was added 50 mg of finely powdered **1b**—**e** with stirring, and the reaction mixture was stirred to provide complete mixing. A small amount of the mixture was taken at an appropriate time interval. One half of the sample was used for measurement of absorbance after dilution with 95.0%-sulfuric acid and another half of the sample was poured into water to precipitate organic materials. These were separated by contrifugation, dried, dissolved in 1% potassium hydroxide, and analyzed by paper chromatography.

Measurements and Calculations. Absorbances were measured with a Hitachi 101 Spectrophotometer. The determination of the reaction mixture and paper chromatography were carried out as in the experiment reported before.1) The calculations of composition or rate ratio $K(=k_2/k_1)$ were made by IBM 370 computer.

Results and Discussion

In the reactions at 180—200 °C, all the reaction mixtures have been proved to contain only three components, **1b**—**e**, **2b**—**e**, and **3** by paper chromatography. The compositions in the reaction mixture were determined by spectroscopy. The contents, $C_I/(C_I+C_M+C_A)$, $C_M/(C_I+C_M+C_A)$, and $C_A/(C_I+C_M+C_A)$ where C_I, C_M, and C_A are the concentrations of **1b**—**e**, **2b**—**e**, and **3**, respectively, were obtained from the standard absorbances of **1b**—**e**, **2b**—**e**, and **3**. Figure 1 shows a typical reaction curve. The pattern was similar in all reactions. As the reactions proceed, the yields of **2b**—**e** initially increased, but decreased after reaching a maximum. The maximum yields of **2b**—**e** were compared. Table 1 gives the maximum yields of **2b**—**e** in the reactions at 180, 190, and 200 °C. It is shown

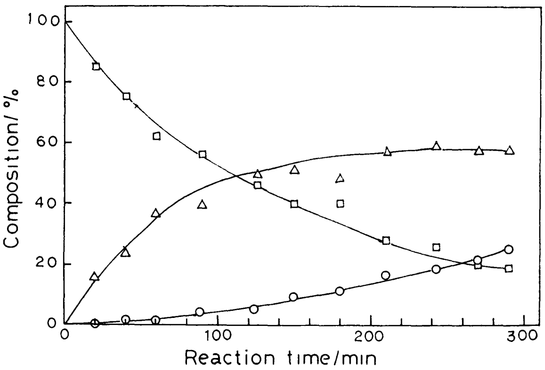


Fig. 1. Reaction of *N,N'*-dipropyl-3,4 : 9,10-perylenebis (dicarboximide) (**1d**) with H$_2$SO$_4$.
Reaction temp: 180 °C. □: *N,N'*-Dipropyl-3,4: 9,10-perylenebis(dicarboximide) (**1d**), △; *N*-Propyl-3,4: 9,10-perylenetracarboxylic monoahydride monoimide (**2d**), ○: 3,4: 9,10-Peryleneteracarboxylic dianhydride (**3**).

Table 1. The maximum yields of *N*-alkyl-3,4: 9,10-perylenetetracarboxylic monoanhydride monoimide (**2b**—**e**)

N,N'-Dialkyl-3,4 : 9,10-perylenebis-(dicarboximide) (**1b**—**e**)	R	Temp °C	Time min	Maximum yield of **2b**—**e** %	
1b	CH$_3$	180	270	44	**2b**
		190	200	48	
		200	100	47	
1c	CH$_2$CH$_3$	180	220	55	**2c**
		190	140	49	
		200	40	45	
1d	CH$_2$CH$_2$CH$_3$	180	240	58	**2d**
		190	80	56	
		200	40	50	
1e	CH$_2$CH$_2$CH$_2$CH$_3$	180	180	53	**2e**
		190	150	47	
		200	40	40	

that all the values are in the range of 40—60%; the value is the smallest in **1b** and increases a little at lower temperature. The yields of **2b**—**e** isolated from the reaction mixture at 180 °C were **2b** : 31%, **2c** : 31%, **2d** : 31%, **2e** : 41%. Thus the yields of separable **2b**—**e** are lower than the spectroscopic yields in Table 1, because of the difficulty of their separation.

There was a scattering of the data points on a reaction curve as the concentration of **1b**—**e** increased over 100 mg/50 ml sulfuric acid; this became more serious at higher temperature, and was the largest in **1b** and the smallest in **1d**. In the reaction of **1a**,[3] no scattering was observed in ten times the concentration (500 mg/50 ml). This was attributed to the fact that the solubility of **1b**—**e**, which has an alkyl group, is smaller than that of **1a**. For these reasons, more sulfuric acid is necessary for the preparation of **2b**—**e** from **1b**—**e** than that from **1a**.

Plots of $\ln(C_I/C_{I0})$, where C_{I0} is the initial concentration of **1b**—**e**, *vs.* time are linear in the reaction of 50 mg **1b**—**e** at 180 °C. The rate constants k_1, for the reaction of **1b**—**e** to **2b**—**e**, were calculated from the slope. The rate ratios $K(k_2/k_1)$, where k_2 is the rate constant of **2b**—**e** to **3**, were calculated from Eq. 1.[1] Most of the values in each reaction were constant. These results indicated that the reaction followed a pseudo-first-order process. The rate constants k_1 and

$$C_M/C_{I0} = \{1/(1-K)\}\{(C_I/C_{I0})^K - (C_I/C_{I0})\} \qquad (1)$$

rate ratio K are given in Table 2. All the rate constants are in the range of 0.45—0.95 × 10^{-2} min^{-1}, and the rate ratio K are in the range of 0.35—0.50. A longer alkyl chain decreased the rate constants and ratios in the condensation of **3** with alkylamine,[1] but there was no such significant effect of alkyl groups in this reaction. All the k_1 values of **1b**—**e** were smaller than that of **1a** ($k_1 = 1.06 \times 10^{-2}$ min^{-1}).[3] Polar substituent constant σ^* are : H : +0.490, CH_3 : 0.000, C_2H_5 : −0.100, *n*-C_3H_7 : −0.115, *n*-C_4H_9 : −0.130.[4] The large k_1 value in **1a** is related to the polar effects of *N*-substituents.

TABLE 2. RATE CONSTANT k_1 AND RATE RATIO $K(=k_2/k_1)$
Reaction temp, 180 °C

N,*N*-Dialkyl-3,4 : 9,10-perylenebis(dicarboximide) (**1b**—**e**)	R	$k_1 \times 10^2$ / min^{-1}	$K(=k_2/k_1)$
1b	CH_3	0.472	0.420
1c	CH_2CH_3	0.929	0.420
1d	$CH_2CH_2CH_3$	0.572	0.360
1e	$CH_2CH_2CH_2CH_3$	0.920	0.500

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