NOTES.

The Cannizzaro Reaction. By ARNOLD WEISSBERGER and RUDOLF HAASE.

A RELATION has already been established between the rates of oxidation of α-ketols and the dissociation constants of the corresponding acids (Weissberger, *Ber.*, 1932, **65**, 1815), and another has now been found between the dissociation constants and the rates of reaction in the Cannizzaro dismutation (Haase, Dissert., Leipzig, 1933).

The experiments were carried out in homogeneous systems: solvent, 75 (wt.) % ethyl alcohol; initial concentration of the aldehyde, 0·4*M*, and of the alkali (sodium hydroxide), 0·2*N*; temperature, 30·0° ± 0·1°. They were followed by titration of the alkali with standard acid. As shown in the table, a relation exists between the rates of the Cannizzaro reaction of the aldehydes, R·CHO, and the dissociation constants (*K*) of the corresponding acids, R·CO$_2$H; *t* is the time (minutes) in which one-quarter of the alkali was neutralised. With *o*-substituted aldehydes, the reaction is slower than would be expected from the dissociation constants, thus indicating the operation of another factor, presumably steric hindrance.

Benzaldehyde.	*t*.	$K \times 10^5$.*	Benzaldehyde.	*t*.	$K \times 10^5$.*
p-Dimethylamino	>50,000	0·94	*m*-Chloro	106	15·5
p-Methoxy	10,000	3·2	*m*-Nitro	26	34·5
p-*iso*Propyl	6,000	5·2	*o*-Ethoxy	15,000	8·6
Unsubstituted	4,470	6·6	*o*-Chloro	9,000	132
p-Chloro	310	9·3	*o*-Nitro	440	606

* Landolt–Börnstein "Tabellen," 5th ed., Berlin, 1923.

On account of its smaller solubility it was impossible to investigate *p*-nitrobenzaldehyde under the same conditions. This compound, therefore, was treated in 0·1*M*-solution with 0·05*N*-alkali. The quarter period was 235 minutes; the dissociation constant of *p*-nitrobenzoic acid is 39·5 × 10^{-5}. The values for the *m*-nitro-compounds under the same conditions are 245 minutes and *K* 34·6 × 10^{-5}.—THE DYSON PERRINS LABORATORY, THE UNIVERSITY, OXFORD. [*Received, November 27th*, 1933.]

Perylene and Derivatives. By GILBERT T. MORGAN and JAMES G. MITCHELL.

THE m. p. of perylene is generally quoted as 264—265°, but the fact that this product sinters below that temperature suggests that some impurity is present; purification has now been effected through the picrate. The perylene employed was prepared by the method described in E.P. 208,722 (comp. Nat. Mat. Col. Prod. Chem.) in which β-dinaphthol is warmed with phosphorus oxychloride and finally distilled in presence of zinc dust. A yield of *ca.* 20% of perylene (m. p. 264—265°) was isolated from the distillate. A warm solution of this product in dry benzene, mixed with picric acid (1 mol.) in the same solvent, threw down dark-coloured needles, m. p. 223—224·5° (perylene content, 52·7. Calc. for $C_{20}H_{12},C_6H_3O_7N_3$, 52·4%); a monopicrate (m. p. 221°) and a dipicrate (m. p. 154—155°) have been described (Brass and Tengler, *Ber.*, 1931, **64**, 1650). Treatment of the picrate with warm water regenerated perylene, which then separated from acetic acid as pale bronze leaflets, m. p. 273—274° (Found : C, 95·1; H, 4·7. Calc. for $C_{20}H_{12}$: C, 95·2; H, 4·8%). No difference in the colour reactions of the pure and the impure hydrocarbon could be detected.

In an attempt to synthesise 1 : 7-perylenequinone, Meldola's method (J., 1885, **47**, 525) for the preparation of 1-iodo-β-naphthol was used. As stated by Meldola, the product of this reaction is extremely sensitive to light; but if dilute acetic acid is used in place of alcohol as crystallising medium, colourless needles (m. p. 94·5°) are obtained, specimens of which remain unaffected for some months. Methoxy-β-naphthol did not react with Meldola's reagent. In boiling pyridine 1-iodo-β-naphthol formed a tar, part of which was soluble in alkali and gave no distinctive colour in concentrated sulphuric acid. The alkali-insoluble part (28%) was free from halogen and exhibited a mauve colour in concentrated sulphuric acid. All efforts to crystallise this material failed, nor could the properties of a quinone be detected. On distillation from zinc dust in a stream of hydrogen three products were observed : (1) naphthalene, (2) a yellow substance (25%), crystallising in flat needles (m. p. 236—239°), subsequently identified as dinaphthalene dioxide, (3) a trace of a red substance; no perylene was detected.

The reaction between β-dinaphthol and aluminium chloride to form 1 : 12-perylenequinone is difficult to control and the yield is poor. If, however, the aluminium salt of β-dinaphthol is heated with three times its weight of aluminium chloride at 140—150°, a slow reaction occurs, the progress of which is marked by the development of a green coloration throughout the mass; yields of 70—80% of the quinone have been obtained by this method. The aluminium salt of the corresponding dinaphthol from Naphthol A.S. (the anilide of 3-carboxy-β-naphthol) on similar treatment gave a green substance forming an orange vat. The product was, however, insoluble in organic solvents and could not be obtained in a pure state.

Unsuccessful attempts were made to simplify the preparation of perylenetetracarboxylic anhydride by condensation of acenaphthene, 4-chloroacenaphthene, naphthalic anhydride, 4-chloronaphthalic anhydride, and other substances with condensing agents such as aluminium chloride, zinc chloride, sodamide, and alkali fusion. The separation of the monoimide and the free tetracarboxylic acid can be accomplished by addition of sodium chloride to a solution of the mixture in dilute alkali; the red monoimide is thus salted out, leaving a clear fluorescent solution of sodium perylenetetracarboxylate.—RESEARCH LABORATORY, TEDDINGTON. [*Received, March 1st*, 1934.]