NOTES.

Naphthalene-1 : 5-*disulphonic Acid as a By-product in the Monosulphonation of Naphthalene.* By CEDRIC BURTON RADCLIFFE and WALLACE FRANK SHORT.

ACCORDING to the literature (Mertz and Weith, *Ber.*, 1870, **3**, 195; Landshoff, G.P. 50411, 1889; Euwes, *Rec. trav. chim.*, 1909, **28**, 298) naphthalene is not disulphonated by concentrated sulphuric acid until a relatively high temperature is attained. In the preparation of 1-naphthonitrile from sodium naphthalenesulphonate and potassium cyanide (Mertz and Muhlhäuser, *Ber.*, 1870, **3**, 709) we obtained as by-product a yellow oil, b. p. 220—245°/3—4 mm., which solidified on trituration with acetone and after repeated crystallisation from alcohol and acetic acid melted at 257° (uncorr.). This substance was shown to be 1 : 5-naphthylene dicyanide by saponification to naphthalene-1 : 5-dicarboxylic acid, m. p. 320—322° (corr.), according to the method of Weissgerber and Kruber (*Ber.*, 1919, **52**, 354). The dimethyl ester of the acid melted at 113—114° (uncorr.) (Moro, *Gazzetta*, 1896, **26**, i, 92). The sodium naphthalene-α-sulphonate was prepared by the sulphonation of naphthalene with 1·96 mols. of sulphuric acid (98%) at 40—50°, followed by conversion into the barium salt. It is evident that owing to the sparing solubility of the barium salt of naphthalene-1 : 5-disulphonic acid and incomplete conversion into the dicyanide, an estimate of the degree of disulphonation based upon the yield of dicyanide (1·4 g. per 100 g. of naphthalene employed) must be a conservative one.—AUCKLAND UNIVERSITY COLLEGE, NEW ZEALAND. [*Received, December* 3*rd*, 1930.]

The Bromination of 4-*Nitro*-1-*methylnaphthalene.* By JOHN STANLEY HERBERT DAVIES and ALBERT EDWARD OXFORD.

AN attempt to prepare 4-nitro-1-naphthylmethyl bromide by brominating the nitro-hydrocarbon in ultra-violet light gave only nuclear-substituted mono- and tetra-bromo-derivatives.

A small quartz flask containing 4-nitro-1-methylnaphthalene (5 g.) and bromine (5 g.) was held over a mercury lamp at such a height that the flask was just warm to the hand. Evolution of hydrogen bromide soon commenced and the mixture became almost fluid and then pasty (2—2½ hours). The almost solid product was washed with ether. By crystallisation from alcohol and mechanical separation, the residue (5 g.) gave *monobromo*-4-*nitro*-1-*methylnaphthalene*, in delicate yellow needles, m. p. 137·5—138·5° (Found: C, 49·6; H, 3·1; N, 5·1; Br, 30·3. $C_{11}H_8O_2NBr$ requires C, 49·6;

H, 3·0; N, 5·3; Br, 30·1%), and a very small amount of *tetrabromo-4-nitro-1-methylnaphthalene* as hard vitreous crystals, m. p. 189—190° (decomp.) (Found: C, 26·4; H, 1·8; N, 2·8; Br, 62·7. $C_{11}H_5O_2NBr_4$ requires C, 26·2; H, 1·0; N, 2·8; Br, 63·6%).

A similar mixture of substances was obtained when bromination was carried out for 2 hours at 100—120° in a sealed tube.

α-Naphthylmethyl chloride has previously been described as a liquid. 1-Methylnaphthalene (100 g.) was chlorinated exactly as described by Wislicenus and Wren (*Ber.*, 1905, **38**, 502); the dark brown product on distillation yielded a first fraction (43 g.), b. p. 128—142°/14—16 mm., and a main fraction (55 g.), b. p. 146—158°/14—16 mm. The latter solidified when cooled to − 15° and separated from alcohol at − 15° in elongated silvery flakes, m. p. 29·5—30·5° (Found: C, 74·9; H, 5·1; Cl, 19·8. Calc. for $C_{11}H_9Cl$: C, 74·8; H, 5·1; Cl, 20·1%).

2 : 4-*Dinitrobenzyl Bromide*.—2 : 4-Dinitrobenzyl chloride was boiled (6 hours) with excess of sodium bromide in methyl alcohol. The filtered solution was evaporated, the resulting oil dissolved in ether, and the ethereal solution allowed to evaporate in the ice-chest. Bushes of delicate colourless needles, m. p. 46—47°, were formed, readily soluble in the usual solvents with the exception of the higher alcohols (Found: Br, 29·9. Calc. for $C_7H_5O_4N_2Br$: Br, 30·7%).—[*Received, October* 24th, 1930.

Reaction of p-*Anisidine and Ethyl Methylacetoacetate.* By WILLIAM OGILVIE KERMACK and JAMES FERGUS SMITH.

THE crystalline solid, m. p. 46°, obtained from ethyl acetoacetate and *p*-anisidine at 37° is without doubt ethyl β-*p*-anisidinocrotonate, $MeO{\cdot}C_6H_4{\cdot}NH{\cdot}CMe{:}CH{\cdot}CO_2Et$ (Conrad and Limpach, *Ber.*, 1888, **21**, 1651).

The following evidence, however, indicates that the white crystalline *compound*, m. p. 51° (from aqueous alcohol) isolated from the semi-solid crystalline mass (compare J., 1930, 2005) obtained from *p*-anisidine and ethyl methylacetoacetate is formed from 2 mols. of the former and 1 mol. of the latter.

(1) Analysis.—Found: N, 7·1, 7·3, 7·4. $C_{14}H_{19}O_3N$ requires N, 5·6%. $C_{21}H_{28}O_4N_2$ requires N, 7·5%.

(2) Whereas the product obtained from equimolecular quantities of *p*-anisidine and ethyl acetoacetate is a hard solid (yield, almost theoretical) after removal of water in a vacuum desiccator, the corresponding product from *p*-anisidine and ethyl methylacetoacetate is only semi-solid even under diverse conditions (yield, 64% of

the theoretical, calculated as $C_{14}H_{19}O_3N$, or 90% calculated as $C_{21}H_{28}O_4N_2$.

(3) When 2 mols. of *p*-anisidine and 1 mol. of ethyl methylacetoacetate are kept at 37°, the mixture after removal of water sets to a hard mass. Yield of crude material, m. p. 40—46°, 95% of the theoretical, calculated as $C_{21}H_{28}O_4N_2$.

(4) When kept in a stoppered tube, but not in a vacuum desiccator, the compound, m. p. 51°, gradually darkens with softening and finally becomes a black liquid, whereas ethyl β-*p*-anisidinocrotonate is a stable compound.

(5) Treatment of the compound of m. p. 51° (5 g.) with acetic anhydride yields aceto-*p*-anisidide, m. p. 125—126° (yield, 3·8 g.). Theoretical yield calculated for $C_{14}H_{19}O_3N$, 3·3 g.; for $C_{21}H_{28}O_4N_2$, 4·4 g.

(6) Molecular weight: 199 and 202 (cryoscopically in benzene). Calculated for $C_{14}H_{19}O_3N,C_7H_9ON$, 186; and for

$$(MeO\cdot C_6H_4\cdot NH)_2CMe\cdot CHMe\cdot CO_2Et,$$

372. This result indicates dissociation of the compound

$$C_{14}H_{19}O_3N,C_7H_9ON$$

in benzene but appears inconsistent with the formula $C_{14}H_{19}O_3N$.

An examination of the literature indicates that certain crystalline condensation products of ethyl and methyl acetoacetates with derivatives of aniline, *e.g.*, *p*-toluidine (Conrad and Limpach, *Ber.*, 1888, **21**, 523), are probably normal derivatives of β-anilinocrotonic acid and analogous to the β-*p*-anisidinocrotonate mentioned above.—RESEARCH LABORATORY, ROYAL COLLEGE OF PHYSICIANS, EDINBURGH. [*Received, November* 6th, 1930.]

An Attempted Preparation of Methanetetrasulphonic Acid. By FREDERIC BARRY KIPPING.

IN an attempt to prepare potassium methanetetrasulphonate, aqueous solutions of potassium di-iodomethanedisulphonate (v. Pechmann, *Ber.*, 1895, **28**, 2379) and potassium sulphite were heated together under reflux during 4—5 hours: on cooling, a crystalline salt separated which was identified as potassium methionate (Found: K, 30·7, 30·8. Calc. for $CH_2O_6S_2K_2$: K, 30·9%). The barium salt was prepared by precipitation with barium chloride (Found: Ba, 39·7. Calc. for $CH_2O_6S_2Ba,2H_2O$: Ba, 39·6%). When hot solutions of the same substances were mixed, a violent reaction occurred and potassium methionate again separated (Found: for potassium salt: K, 30·9, and for barium salt: Ba, 39·9, 39·8; H_2O, 10·3. Required for $2H_2O$, 10·35%). The identity of the potassium salt with potassium methionate (prepared by the interaction of acetylene and fuming sulphuric acid and lent to me by Dr. F. G. Mann) was also proved by taking *X*-ray rotation photographs with the length of the crystals as the rotation axis. For these photographs I am greatly indebted to Dr. Wooster and Mr. Bernal.

During this work attempts were made to prepare potassium methionate, for purposes of comparison, by the sulphonation of acetamide with fuming sulphuric acid (Buckton and Hofmann, *Annalen*, 1856, **100**, 133). When acetamide was heated with fuming acid containing about 65% or 30% of sulphur trioxide at various temperatures, the product obtained in every case was potassium methanetrisulphonate (Found: K, 30·1, 30·0; H_2O, 4·8. Calc. for $CHO_9S_3K_3,H_2O$: K, 30·15; H_2O, 4·6%). With acid containing 10% of sulphur trioxide, below about 170—180° no product but potassium acetate could be isolated, but after heating to 210° potassium methionate was obtained in somewhat poor yield (Found: K, 30·8%; H_2O, none). The fuming acid used by Buckton and Hofmann (about which they give no details) was therefore apparently fairly dilute, as there seems no doubt that they actually obtained methionic acid. Backer (*Rec. trav. chim.*, 1930, **49**, 1108) has converted methionic acid into methanetrisulphonic acid by treatment with fuming sulphuric acid, an experiment which probably explains the difference in the products obtained from acetamide.

While the first stages of this work were in progress the interaction of potassium diazomethanedisulphonate (v. Pechmann, *loc. cit.*) and potassium sulphite was studied and the product identified as potassium methanetrisulphonate (Found: K, 30·15; H_2O, 4·9%. Found in dried material: K, 31·6%). The conclusion of Fantl and Fisch (*J. pr. Chem.*, 1930, **124**, 159) and Backer and Klaassens (*Rec. trav. chim.*, 1930, **49**, 1047, 1110) concerning the non-existence of hydroxymethanetrisulphonic acid (*Ber.*, 1895, **28**, 2382; *Annalen*, 1872, **161**, 139) had already been reached before my attention was drawn to the recent papers. This conclusion is therefore fully confirmed.—THE UNIVERSITY, CAMBRIDGE.

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