

NOTES.

p-Aldehydophenyltrimethylammonium Salts and their Condensation and Decomposition Products.
By AHMAD ZAKI and WADIE TADROS.

p-Aldehydophenyltrimethylammonium Salts.—The *picrate* was precipitated in golden-yellow plates or feathery crystals when aqueous solutions of picric acid and of the dark red product obtained from the interaction of methyl sulphate and *p*-dimethylaminobenzaldehyde (Zaki, J., 1930, 1078. It is not necessary to isolate the *p*-aldehydophenyltrimethylammonium methosulphate) were mixed. Recrystallised twice from hot water (charcoal), the picrate had m. p. 169°. Yield, 50% (Found: C, 48.9; H, 4.0; N, 13.8. $C_{16}H_{16}O_8N_4$ requires C, 49.0; H, 4.1; N, 14.3%).

Chloride. The picrate was warmed with concentrated hydrochloric acid. After cooling, the precipitated picric acid was removed, the filtrate washed with ether or benzene and evaporated to dryness, and the residue crystallised from absolute alcohol, the *chloride* separating in colourless crystals, m. p. 191°, readily soluble in water and warm 96% ethyl alcohol, insoluble in ether, benzene, and acetone (Found: C, 60.1; H, 7.1; N, 7.1; Cl, 17.8. $C_{10}H_{14}ONCl$ requires C, 60.1; H, 7.1; N, 7.0; Cl, 17.8%). Addition of ether to the alcoholic mother-liquor precipitated a second crop of the chloride.

Iodide. (a) A mixture of *p*-dimethylaminobenzaldehyde (10 g.) and excess of methyl iodide (50 g.) was refluxed for 15—20 hours, and the excess then recovered by distillation. When the residue was washed with ether, the *iodide* was obtained in colourless crystals. (b) When saturated aqueous solutions of the above chloride and potassium iodide were mixed, the iodide separated in colourless crystals, m. p. 164—165°, soluble in water and hot alcohol, insoluble in ether, benzene, and acetone (Found: I, 43.1. $C_{10}H_{14}ONI$ requires I, 43.6%).

The perchlorate, precipitated on addition of a few c.c. of 30% perchloric acid solution to a concentrated aqueous solution of the chloride, crystallised from water in colourless plates, m. p. 143° (Found: Cl, 13.4. Calc. for $C_{10}H_{14}O_5NCl$: Cl, 13.5%).

Chloride perbromide. Solutions of a slight excess of bromine (3.5 g.) and the chloride (3 g.) in acetic acid (10 c.c. each) were mixed and left overnight in the ice-chest. The precipitated perbromide separated from acetic acid in orange-red crystals, m. p. 115—116°. It was unstable and the colour disappeared entirely within 8—10 weeks.

Condensation Products.—(1) A mixture of the iodide (1 g.), hydroxylamine hydrochloride (1.2 g., dissolved in the least quantity of water), sodium carbonate (1 g.), and absolute alcohol (10 c.c.) was refluxed for 3 hours, and the alcohol then distilled off from the filtered solution. To an aqueous solution of the residue aqueous picric acid was added, precipitating the *picrate* of the *oxime*, which crystallised from water in yellow needles, m. p. 201—202° (Found: C, 47.6; H, 4.5; N, 17.4. $C_{16}H_{17}O_8N_5$ requires C, 47.2; H, 4.3; N, 17.2%).

(2) The *picrate* of the *semicarbazone*, obtained in the same way (iodide, 2 g.; semicarbazide hydrochloride, 0.9 g.; sodium acetate, 0.6 g.; absolute alcohol, 10 c.c.), separated from water in orange-yellow crystals, m. p. 227—228° (Found: C, 45.6; H, 4.3; N, 21.7. $C_{17}H_{19}O_8N_7$ requires C, 45.4; H, 4.2; N, 21.8%).

(3) The *picrate* of the *phenylhydrazone*, also obtained similarly (iodide, 1 g.; phenylhydrazine hydrochloride, 0.7 g.; sodium acetate, 0.5 g.; absolute alcohol, 20 c.c.), crystallised from dilute alcohol in orange-yellow needles, m. p. 200—201°, very sparingly soluble in water (Found: C, 54.2; H, 4.5; N, 17.5. $C_{22}H_{22}O_7N_6$ requires C, 54.8; H, 4.6; N, 17.4%).

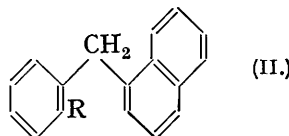
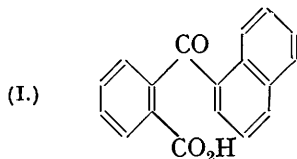
(4) A mixture of the chloride (3 g.) and *m*-nitroaniline (3 g.) was heated at 160—165° for an hour. The product was dissolved in water, and picric acid added to the filtered solution. The voluminous *picrate* of the condensation product crystallised from dilute alcohol in reddish-brown needles, m. p. 208° (Found: C, 50.7; H, 4.1; N, 16.8. $C_{22}H_{20}O_9N_6$ requires C, 51.4; H, 3.9; N, 16.4%).

Decomposition of the Chloride.—A mixture of the chloride (2 g.) and alcoholic sodium ethoxide (0.5 g. of sodium in 40 c.c. of absolute alcohol) was refluxed for 3 hours. After dilution with water, the solution was extracted with ether. The extract contained two components: (a) *p*-dimethylaminobenzaldehyde (0.48 g.), m. p. and mixed m. p. 73°, separated by shaking with dilute hydrochloric acid; (b) *p*-ethoxybenzaldehyde (0.75 g.), obtained as a brownish oily residue after evaporation of the ether. [The influence of the aldehyde-group in producing the latter type of fission is shown by comparison with the decomposition of phenyltrimethylammonium and phenylbenzyltrimethylammonium chlorides by alcoholic sodium ethoxide (Vorländer and Spreckels, *Ber.*, 1919, 52, 309); in both these cases one route is followed, yielding dimethylaniline.] The latter was oxidised by alkaline potassium permanganate to *p*-ethoxybenzoic acid, m. p. 195° (Gattermann, *Annalen*, 1907, 357, 348). The alkaline solution was freed from ether by warming and just acidified with acetic acid; a trace of *p*-dimethylaminobenzoic acid, m. p. and mixed m. p. 233°, was the only precipitate.—FOUAD I UNIVERSITY, CAIRO, EGYPT. [Received, May 5th, 1941.]

Derivatives of o-1-Naphthoylbenzoic Acid and 1-Benzyl-naphthalene-2'-carboxylic Acid.

By G. M. BADGER.

IN connection with a scheme, now indefinitely postponed, for the synthesis of certain complex fluorene derivatives, the Curtius degradation has been attempted with *o*-1-naphthoylbenzoic acid (I). The ethyl ester of this acid reacted with hydrazine hydrate to form 4-*keio*-1-(1'-*naphthyl*)-3 : 4-dihydrophthalazine. However, the reduced acid, 1-benzyl-naphthalene-2'-carboxylic acid (II, R = CO₂H), was successfully degraded to 1-*o*-aminobenzyl-naphthalene.



Ethyl *o*-1-naphthoylbenzoate, prepared from the acid (2 g.) by 7 hours' boiling with alcohol (50 c.c.) and sulphuric acid (1 c.c.), formed colourless transparent prisms, m. p. 81.5—83° (Found: C, 78.65; H, 5.4. Calc. for $C_{20}H_{16}O_3$: C, 78.9; H, 5.3%). Graebe (*Annalen*, 1905, 340, 251) gives m. p. 123—124°. The m. p. now recorded was obtained with specimens of ester prepared from the pure acid, m. p. 172—174°, synthesised from phthalic anhydride either by treatment with naphthalene in the presence of aluminium chloride (Graebe, *loc. cit.*) or with 1-naphthylmagnesium bromide (Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1937, 59, 1028). The methyl ester, prepared by the action of diazomethane on *o*-1-naphthoylbenzoic acid, had m. p. 119—120°, in agreement with Graebe.

4-*Keto*-1-(1'-*naphthyl*)-3 : 4-dihydrophthalazine (4.4 g.) was obtained by 6 hours' heating at 120° of a mixture of ethyl *o*-1-naphthoylbenzoate (5 g.), hydrazine hydrate (5 c.c.), and absolute alcohol (10 c.c.). Recrystallised from xylene and from acetic acid, it formed colourless crystals, m. p. 252—253° (Found: C, 79.5; H, 4.6. $C_{16}H_{12}ON_2$ requires C, 79.4; H, 4.45%).

o-1-Naphthylmethylbenzhydrazide (II; R = CO·NH·NH₂).—A solution of 1-benzyl-naphthalene-2'-carboxylic acid (10 g.) in absolute alcohol (300 c.c.) and sulphuric acid (8 c.c.) was refluxed for 5 hours. The colourless oil obtained was treated with hydrazine hydrate (10 c.c.)

and absolute alcohol (10 c.c.) and heated at 120° for 10 hours. The *hydrazide* formed colourless silky needles (8.0 g.), m. p. 175—176° (Found : C, 78.0; H, 5.85. $C_{18}H_{16}ON_2$ requires C, 78.2; H, 5.8%).

ω -1-*Naphthyl-o-tolylurethane* was obtained by gradual addition of sodium nitrite (2.2 g.) in water (10 c.c.) to a stirred solution of the above hydrazide (3.6 g.) in acetic acid (100 c.c.) and concentrated hydrochloric acid (10 c.c.) at 10°. After 1 hour, the solution was diluted with water (100 c.c.). The thick oil obtained was collected, dissolved in warm alcohol, and boiled for $\frac{3}{4}$ hour. The *urethane* formed colourless needles from alcohol, m. p. 113—114° (Found : C, 78.5; H, 6.2. $C_{20}H_{18}O_2N$ requires C, 78.65; H, 6.25%).

Hydrolysis of the urethane (0.5 g.) with concentrated aqueous ammonia (10 c.c.) in a sealed tube at 180° for 2 hours gave 1-*o-aminobenzyl-naphthalene* (II, R = NH₂) in colourless needles, from alcohol, m. p. 101—102° (Found : C, 87.4; H, 6.25. $C_{17}H_{15}N$ requires C, 87.5; H, 6.4%).

My thanks are due to Professor J. W. Cook, F.R.S., for his interest in this work, to the Finney-Howell Research Foundation for a fellowship, and to the British Empire Cancer Campaign for a grant to this Institute.—THE CHESTER BEATTY RESEARCH INSTITUTE, THE ROYAL CANCER HOSPITAL (FREE), LONDON, S.W. 3. [Received, May 19th, 1941.]

Action of Alkaline-earth Chlorides on Emulsions stabilised by Sodium Oleate. By A. H. ADAMS and A. R. MARTIN.

FROM experiments on the partial coagulation of a standard emulsion in sodium oleate solution by salts of bi- and higher-valent metals, Martin and Hermann (*Trans. Faraday Soc.*, 1941, **37**, 30) concluded that the extent to which the interfacial film of acid-soap is destroyed by the formation of sols of metal-soap in the organic liquid peptised by oleic acid from the film is an important factor in determining the volume of oil thrown out. They found that the coagulating powers of the alkaline-earth chlorides were in the order Ba > Sr > Ca, but gave no analyses supporting their conclusion in the case of these salts. We have therefore broken their standard benzene emulsion with quantities of the alkaline-earth chlorides equivalent to the sodium oleate present in exactly the manner described by them, and analysed the yellowish oil left after evaporation of the separated benzene, and also the suspension in the aqueous phase. The results, each the mean of two determinations, were as follows, r being the ratio of oleic acid molecules (including oleate expressed as oleic acid) to metal atoms :

Reacting salt.	Oil from benzene.		Suspension in water.	
	Wt. (g.).	r .	Wt. (g.).	r .
CaCl ₂	4.00	2.17	0.84	1.38
SrCl ₂	4.20	2.28	0.83	0.93
BaCl ₂	4.34	2.65	0.66	0.43

The oil phase contains the greater part of the reaction product, in which the ratio of oleic acid to metal exceeds that for the normal oleate. Moreover, this excess follows the same order as the coagulating powers of the salts, Ba > Sr > Ca. The conclusion of Martin and Hermann is therefore true also for the alkaline-earth chlorides.—SIR JOHN CASS INSTITUTE, JEWRY ST., ALDGATE, LONDON, E.C. 3. [Received, May 5th, 1941.]