NOTES.

An ***Improved*** *Method of Nitrating Aromatic* o-*Hydroxy-carboxylic Acids and their Esters.*

By H. C. BARANY and M. PIANKA.

THE following modification appears to be an improvement on the methods stated in the literature (Huebner, *Annalen*, 1879, **195**, 7; Deninger, *J. pr. Chem.*, 1905, **42**, 550; Hirsch, *Ber.*, 1900, **33**, 3239; Meldola, Foster, and Brightman, *J.*, 1917, **111**, 536; Raiziss and Proskouriakoff, *J. Amer. Chem. Soc.*, 1922, **44**, 791; Meldrum and Hirve, *J. Indian Chem. Soc.*, 1928, **5**, 95; Gough and King, *J.*, 1930, **137**, 686; Baroni and Kleinau, *Monatsh.*, 1936, **68**, 258; Koenig, *Ber.*, 1890, **23**, 806; Dye, *J.*, 1915, **107**, 1625) for nitrating aromatic *o*-hydroxy-carboxylic acids and their esters. It employs as nitration agent a 10% solution of nitric acid (*d* 1·42) in glacial acetic acid. Distillation of this mixture afforded a fraction, b. p. 128—130°, which seemed to be diacetylorthonitric acid (Pictet, *Chem. Zentr.*, 1902, II, 1438; *Ber.*, 1902, **35**, 2526). The procedure was to dissolve 1 mole of the compound in the smallest amount of glacial acetic acid and add rapidly, at room temperature, a mixture of 1 mole of nitric acid (*d* 1·42) in 9 times its volume of glacial acetic acid, then warm the reaction mixture until it became brown, cool it, and precipitate the nitro-compound with excess of water. In all cases except in that of 2-hydroxy-3-naphthoic acid the nitro-group was found to be in a position *para* to the hydroxyl group.

The following were prepared : 5-Nitrosalicylic acid, white needles from water, m. p. 228° (yield, 41%); methyl 5-nitrosalicylate, white needles from ether, m. p. 96° (yield, 51%); ethyl 5-nitrosalicylate, obtained from the reaction mixture on standing, yellow needles, m. p. 98—99° (yield, 64%); 4-nitro-1-hydroxy-2-naphthoic acid, pale yellow needles from dilute acetone, m. p. 214° (yield, 69·5%); 4-nitro-3-hydroxy-2-naphthoic acid, orange crystals from ether, m. p. 233—234° (yield, 49%); methyl 4-nitro-1-hydroxy-2-naphthoate, pale yellow needles from benzene, m. p. 161° (yield, 77·3%); *ethyl* 4-*nitro*-1-*hydroxy*-2-*naphthoate*, pale yellow needles from benzene, m. p. 87—88° (yield, 86%) (Found : C, 59·82; H, 4·13; N, 5·41. $C_{13}H_{11}O_5N$ requires C, 59·77; H, 4·21; N, 5·36%); *propyl* 4-*nitro*-1-*hydroxy*-2-*naphthoate*, pale yellow needles from benzene–light petroleum, m. p. 117—118° (yield, 87%) (Found : C, 60·87; H, 4·82; N, 5·00. $C_{14}H_{13}O_5N$ requires C, 61·09; H, 4·72; N, 5·09%).

Melting points are uncorrected.—RESEARCH LABORATORIES, DUFAY-CHROMEX LIMITED, ELSTREE, HERTS. [*Received, April 5th,* 1946.]

Amides Derived from ω-Chloroacetophenone. By WILLIAM A. WATERS.

THE water-soluble aromatic amines derived from ω-chloroacetophenone have a pungency which is not unlike that of capsaiacin. Since the maximum pungency in the acylvanillylamide (capsaiacin) series is found in an amide of one particular chain-length (compare Ford-Moore and Phillips, *Rec. Trav. chim.*, 1934, **53**, 847), it was of interest to prepare a number of acylamido-ω-chloroacetophenones, and to investigate both their lachrymatory characters and their pungency in aqueous solution. Both these properties, however, decreased as the chain-length of the amide increased. The following *compounds* were prepared, by standard methods, in the course of this investigation.

ω-*Chloro*-4-*acylamidoacetophenones.*

		Analyses.					
		Found.			Required.		
Acyl group.	M. p.	C, %.	H, %.	Cl, %.	C, %.	H, %.	Cl, %.
Propionyl	208°	58·4	5·33	16·0	58·5	5·32	15·7
n-Butyryl	178	60·0	5·86	14·9	60·1	5·85	14·8
*iso*Butyryl	149	60·2	6·08	14·3	60·1	5·85	14·8
n-Valeryl	175	61·6	6·29	14·4	61·5	6·31	14·0
*iso*Hexoyl	171	63·8	7·11	12·9	62·8	6·73	13·3
n-Octoyl	127	65·0	7·70	12·0	65·1	7·46	12·0
n-Pelargonyl	116	65·7	7·75	11·8	65·9	7·81	11·5
n-Lauryl	114	69·0	8·4	9·6	68·3	8·53	10·1
Myristyl	119	70·1	9·14	9·49	69·6	8·96	9·34
Stearyl	111	71·1	9·91	8·6	71·5	9·64	8·1
Undecenoyl	105	68·4	7·39	10·7	68·0	7·75	10·6
β-Chloropropionyl	201	50·4	4·47	27·0	50·8	4·23	27·3

ω-*Chloro*-3-*acylamidoacetophenones.*

		Analyses.					
		Found.			Required.		
Acyl group.	M. p.	C, %.	H, %.	Cl, %.	Cl, %.	H, %.	Cl, %.
Propionyl	136°	58·8	5·87	15·5	58·5	5·33	15·7
n-Butyryl	93	60·4	5·82	15·1	60·1	5·85	14·8
*iso*Butyryl	136	60·3	5·65	14·8	60·1	5·85	14·8
n-Valeryl	95	61·9	6·52	14·1	61·5	6·31	14·0
*iso*Hexoyl	106	62·9	6·8	13·6	62·8	6·73	13·3
n-Octoyl	96	65·1	7·40	11·7	65·1	7·46	12·0
n-Pelargonyl	91	66·1	7·73	11·5	65·9	7·81	11·5
n-Lauryl	96	68·6	8·89	9·84	68·6	8·53	10·1
Myristyl	100	70·3	9·8	8·9	69·6	8·96	9·3
Undecenoyl	92	68·1	7·96	11·1	68·0	7·75	10·6
β-Chloropropionyl	145	50·7	4·23	27·1	50·8	4·23	27·3

The Chief Scientific Officer of the Ministry of Supply is thanked for permission to publish this Note.—CHEMICAL DEFENCE RESEARCH DEPARTMENT, MINISTRY OF SUPPLY. [*Received, February* 14*th,* 1946.]

Synthesis of Acenaphthene. Part II. By ALEXANDER SCHÖNBERG, RADWAN MOUBASHER, and AKILA MOSTAFA.

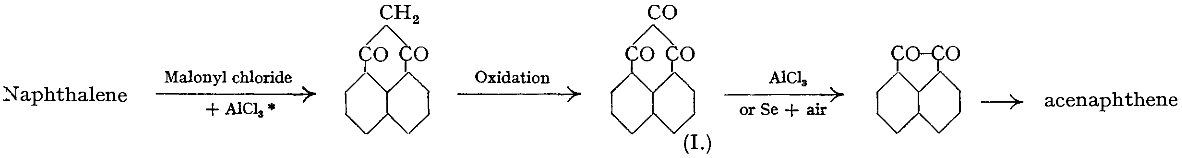
SCHÖNBERG and Moubasher (*J.*, 1939, 1429) have shown that, when diphenyl triketone is heated with anhydrous aluminium chloride and the reaction product decomposed with dilute hydrochloric acid, benzil is obtained.

We have now found that benzil can also be obtained from diphenyl triketone by heating it with selenium in the presence of air, and, further, that acenaphthenequinone is obtained when *peri*naphthanetrione (I) is treated with either aluminium chloride or selenium in the presence of air.

Schönberg (*Ber.*, 1921, **54**, 2838) has shown that acenaphthene can easily be obtained from acenaphthenequinone disemicarbazone by the action of sodium ethoxide; we are therefore now able to advance an easy way of preparing acenaphthene from naphthalene without pyrolysis.

It has been stated (Richter–Anschütz, " Chemie der Kohlenstoffverbindungen," 12th Edition, Vol. II, Part 2, p. 739, Leipzig, 1935) that acenaphthenequinone is easily prepared by the action of oxalyl chloride on naphthalene in the presence of aluminium chloride. The above paper of Schönberg (*loc. cit.*) is given as authority for this statement; it is, however, true only for derivatives of acenaphthenequinone.

Action of selenium in the presence of air on peri*naphthanetrione hydrate.* 0·4 G. of the hydrate (Errera, *Gazzetta*, 1913, **43**, 583) was mixed with 1·5 g. of precipitated selenium (Kahlbaum) in a test tube (25 cm. long) and heated in an oilbath kept at 250°. Heating was continued for two hours, during which a stream of air was constantly passed through a delivery tube which almost touched the surface of the reaction mixture. Acenaphthenequinone sublimed (60% yield). The crude product was identified after recrystallisation by m. p. and mixed m. p. with an authentic specimen, and also by m. p. and mixed m. p. of the condensation products of *o*-phenylenediamine with the reaction product and with an authentic sample of acenaphthenequinone.



* Fleischer and Retze, *Ber.*, 1922, **55**, 3280.

Action of aluminium chloride on peri*naphthanetrione* (I). A mixture of 5 g. of pulverised anhydrous aluminium chloride and 1 g. of *peri*naphthanetrione (Errera, *loc. cit.*) was heated in a long test tube closed with a calcium chloride tube (bath temperature, 220°). A sublimate was formed, and after 30 minutes was put back into the reaction mixture. 30 Minutes later, the contents of the tube were cooled, treated with ice-cold dilute hydrochloric acid, and left for 12 hours. The solid product was washed with water, dried, and crystallised from toluene. Acenaphthenequinone (yield, 0·3 g.) was identified as above.

Action of selenium in the presence of air on diphenyl triketone. The experiment was carried out as in the case of *peri*-naphthanetrione hydrate, using 0·5 g. of diphenyl triketone and 4 g. of selenium. The reaction product formed long needles on the cooler part of the reaction vessel, and without crystallisation melted at 95°. The mixed m. p. (with a sample of benzil) was not depressed.—FOUAD I UNIVERSITY, CAIRO, EGYPT. [*Received, March 26th,* 1946.]