XLII.—*Some Derivatives of Phenylmethacrylic Acid.*

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In the *Berichte* for 1887 (p. 616) I described some derivatives of phenylmethacrylic acid and phenylisobutyric acid, and I have since obtained some further derivatives.

Paranitrophenylisobutyric Acid, $C_6H_4(NO_2)\cdot CH_2\cdot CH(CH_3)\cdot COOH$.

Phenylisobutyric acid, obtained by Conrad and Bischoff's method, is gradually added in small portions to six times its weight of nitric acid, sp. gr. 1·52. On pouring the mixture into cold water, the nitro-

acid is precipitated, and after several crystallisations from alcohol forms small prisms melting at 121°. It is readily soluble in alcohol and acetic acid, but only very slightly in benzene and light petroleum.

Analysis gave—

	$C_{10}H_{11}NO_4$.	I.	II.
C.....	57·42	57·45	—
H.....	5·26	5·43	—
N.....	6·70	—	6·88
O.....	30·62	—	—

The acid forms salts with the alkalis and with barium and strontium, all of which dissolve readily in water. The silver salt is very insoluble. Its analysis gave, dried at 100°, 34·28 per cent. Ag. $C_{10}H_{10}NO_4$ requires 34·21 per cent. Ag.

Oxidation with permanganate yielded an acid which was identified as paranitrobenzoic acid.

Along with the paranitrophenylisobutyric acid of melting point 121° is an acid which remains liquid at the ordinary temperature, and could not be crystallised even on cooling to a low temperature. It forms salts which resemble those of paranitrophenylisobutyric acid, but they are less stable. The silver salt contains 1 mol. H_2O, and is decomposed at 100°; dried over sulphuric acid, it gave 32·49 per cent. Ag; the acid $C_{10}H_{10}NO_4 + OH_2$ requires 32·33 per cent. On oxidation, this acid yields orthonitrobenzoic acid. The liquid acid is, therefore, orthonitrophenylmethacrylic acid.

In order, if possible, to obtain this nitro-acid in a crystalline state, I nitrated the methyl salt, $C_6H_5{\cdot}CH_2{\cdot}CH(CH_3){\cdot}COOCH_3$; it is a liquid boiling at 232°.

Analysis gave—

	$C_{11}H_{14}O_2$.	
C.....	74·16	74·35
H.....	7·86	7·90

This was dropped slowly into fuming nitric acid, sp. gr. 1·54, precipitated by much water, and crystallised from ether. The product separated in long prisms, melting at 76°, easily soluble in ordinary solvents. The analysis shows that, in this case, it is converted into a dinitro-derivative.

The results were as follows:—

	$C_{11}H_{12}N_2O_6$.	I.	II.
C.....	49·25	49·26	—
H.....	4·48	4·59	—
N.....	10·45	—	10·45
O.....	35·82	—	—

On warming this nitro-derivative with sulphuric acid for a few minutes, and diluting with water, the acid is liberated, and forms colourless six-sided prisms, somewhat flattened. It melts at 89°, and is very soluble in ordinary solvents.

Analysis gave—

	$C_{10}H_{10}N_2O_6$.	I.	II.
C.....	47·24	47·09	—
H.....	3·92	4·11	—
N.....	11·02	—	11·20
O.....	37·80	—	—

Nitroamidophenylisobutyric Acid,
$NO_2 \cdot C_6H_3(NH_2)CH_2 \cdot CH(CH_3)COOH$,

is obtained from the dinitro-acid by reduction with ammonium sulphide. It crystallises from hot water in bright-red plates which melt at 138°.

Analysis gave :—

	$C_{10}H_{12}N_2O_4$.	I.	II.
C.....	53·57	53·40	—
H.....	5·36	5·48	—
N.....	12·50	—	12·68
O.....	28·57	—	—

Amidomethylhydrocarbostyril, $C_{10}H_{12}N_2O$.

On boiling the nitroamidophenylisobutyric acid with ammonium sulphide for two hours, a substance was obtained which no longer dissolved in ammonia.

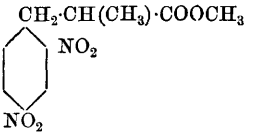
It crystallised from water in slender needles, which melted at 216°, and dissolved with great difficulty in alcohol and light petroleum.

Analysis gave—

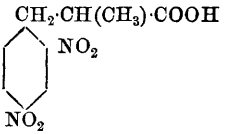
	$C_{10}H_{12}N_2O$.	I.	II.
C.....	68·18	68·30	—
H.....	6·82	7·01	—
N.....	15·91	—	15·95
O.....	9·09	—	—

The formation of this compound leads to the conclusion that one of the nitro-groups in this *dinitrophenylisobutyric acid* is ortho to the fatty part, whilst the second nitro-group is either para or meta. An experiment in which *paranitrophenylisobutyric* was heated with fuming nitric acid produced the same dinitro-acid as above described. The second nitro-group is, therefore, in the para-position to the methane residue.

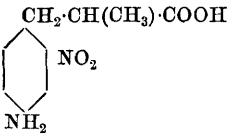
The following formulæ may, therefore, be given as expressing the constitution of these four compounds:—



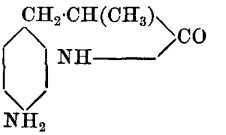
Methyl paraorthodinitrophenylisobutyrate.



Paraorthodinitrophenylisobutyric acid.



Paramido-orthonitrophenylisobutyric acid.



Paramidomethylhydrocarbostyril.

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