

Citation:

Blanksma, J.J., On the constitution of VAN GEUNS'S oxymethyldinitro-benzonitrile., in:
KNAW, Proceedings, 10 II, 1907-1908, Amsterdam, 1908, pp. 509-511

$$\begin{array}{ll}
 P1 = (c, -d, -a, 0, -g, h) & Q1 = (d, c, 0, -a, -h, -g) \\
 P2 = (d, c, 0, -a, h, g) & Q2 = (c, -d, -a, 0, g, -h) \\
 P3 = (0, -f, g, -h, -a, 0) & Q3 = (f, 0, h, g, 0, -a) \\
 P4 = (f, 0, -h, -g, 0, -a) & Q4 = (0, -f, -g, h, -a, 0) \\
 P5 = (g, -h, 0, f, c, -d) & Q5 = (h, g, -f, 0, d, c) \\
 P6 = (h, g, f, 0, -d, -c) & Q6 = (g, -h, 0, -f, -c, d)
 \end{array}$$

if besides is satisfied

$$ch + dg = af - gh = 0.$$

The peculiarity appearing with this example taken for simplicity's sake, that the right lines show mutually some incidences, is lost by submitting the coordinates in Sp_5 first to a linear transformation.

In the same way, indeed, we can formulate for all $Cff.$ indicated in spaces of a lower number of dimensions an analytical definition by deducing the coordinates of their elements from those of the elements of K^{VII} .

Chemistry: — “*On the constitution of VAN GEUNS's oxymethyl-dinitro-benzonitrile*”. By Dr. J. J. BLANKSMA. (Communicated by Prof. A. F. HOLLEMAN).

By the action of potassiumcyanide on meta-dinitrobenzene in methylalcoholic or ethylalcoholic solution, LOBRY DE BRUYN¹⁾ obtained in 1882 the oxymethyl- or oxyethylnitrobenzonitrile $C_6H_3(OCH_3)CNNO_2$, 1. 2. 3.

The investigation of these substances was continued afterwards by VAN GEUNS²⁾ who succeeded in saponifying these nitriles to acid-amines and in preparing the corresponding acids thereof. At the same time VAN GEUNS showed that in both substances a further nitro-group can be introduced by nitration with nitric and sulphuric acids thus yielding the compounds $C_6H_2(OCH_3)CN(NO_2)_2$, m.p. 113° and $C_6H_2(OC_2H_5)CN(NO_2)_2$, m.p. 63°. These two compounds contain a movable nitro-group which may be readily replaced by OH, OCH_3 , NH_2 , $NHCH_3$, NHC_6H_5 , etc.

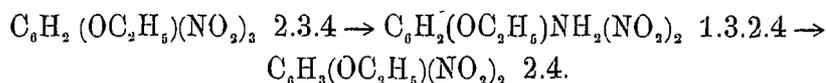
As, however, the place where the nitro-group had been introduced had remained unknown, the constitution of these derivatives was consequently also unknown.

When VAN GEUNS, owing to his departure for India was obliged

¹⁾ Recueil 2, 205.

²⁾ Dissertation Amsterdam 1903.

to discontinue this research I tried at the request of the late Prof. LOBRY DE BRUYN to determine this constitution. After a few trials which led to no result the method was followed which had proved successful in the determination of the constitution of 2.3.4 trinitrophenetol¹⁾. The constitution of that substance was shown to be :



Oxymethyldinitrobenzotrile was now treated in an analogous manner; by the action of alcoholic ammonia one NO_2 -group was replaced by NH_2 and this was then in turn removed by diazotation and boiling with alcohol. In this manner was obtained an oxymethylnitrobenzotrile (m.p. 126°) $\text{C}_6\text{H}_2(\text{OCH}_3)\text{CN}(\text{NO}_2)_2 \rightarrow \text{C}_6\text{H}_2(\text{OCH}_3)\text{CN.NH}_2\text{NO}_2 \rightarrow \text{C}_6\text{H}_3(\text{OCH}_3)\text{CN.NO}_2$.

This shows that the NO_2 -group at 3 is replaced by NH_2 as otherwise the original oxymethylnitrobenzotrile $\text{C}_6\text{H}_3(\text{OCH}_3)\text{CN.NO}_2$ 1.2.3 m.p. 171° would have been reobtained. Now it remained only to determine the constitution of this substance. On treatment with nitric and sulphuric acids an oxymethyldinitrobenzotrile was obtained which melts at 71° and which possesses the following constitution: $\text{C}_6\text{H}_2(\text{OCH}_3)\text{CN}(\text{NO}_2)_2$ 1.2.4.6²⁾.

The constitution of this substance was determined in the following manner. If this compound is treated in alcoholic solution with ammonia or methylamine the OCH_3 group is readily substituted by NH_2 or NHCH_3 and dinitrocyano-aminobenzene m.p. 219° or dinitrocyano-methylaminobenzene m.p. 161° is formed which substances were prepared previously from the corresponding oxyethyl compound³⁾.

The oxymethylnitrobenzotrile m.p. 126° was then heated at 150° with hydrochloric acid for 5 hours. On opening the tube a gas escaped which burnt with a green-bordered flame (CH_3Cl) whilst in the tube there were present crystals which after recrystallisation from water melted at 228° and proved to be 5-nitrosalicylic acid ($\text{C}_6\text{H}_3\text{COOH, OH, NO}_2$. 1. 2. 5.) In the motherliquor the presence of NH_3 was detected, formed by saponification of the cyano-group. For the purpose of identifying the substance obtained a little of the preparation was mixed with an equal quantity of 5-nitrosalicylic acid (m.p. 228° prepared by nitration of salicylic acid⁴⁾). The melting point

¹⁾ Recueil 27, 49.

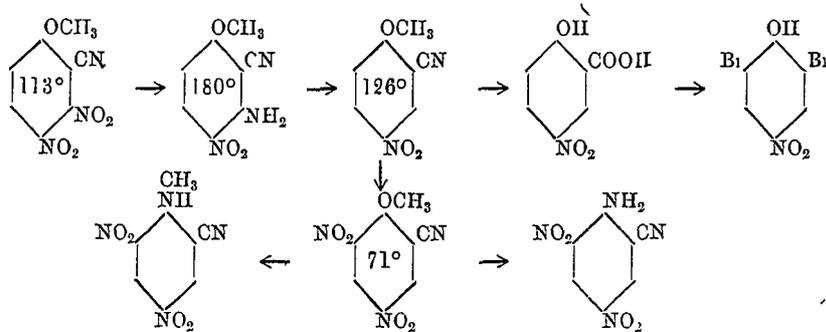
²⁾ This shows that in oxymethylnitrobenzotrile m.p. 126° the nitro-group is placed on 4 or 6.

³⁾ BLANKSMA. Rec. 20, 413. 21, 274.

⁴⁾ HÜBNER. Ann. 195, 31.

was not altered thereby. Both preparations could also be converted readily into 2,6-dibromo-4-nitrophenol m.p. 141° by treatment with bromine water¹⁾.

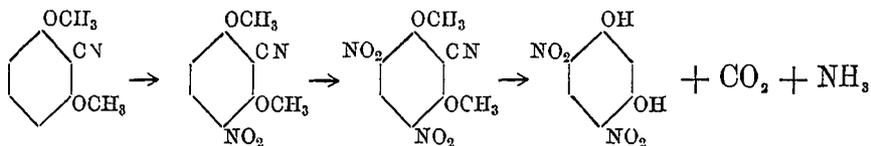
The following reactions were applied:



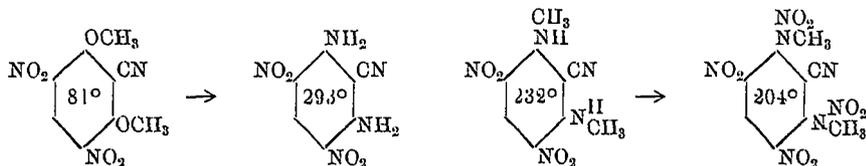
This proved that the constitution of the oxymethyldinitrobenzonitrile prepared by VAN GEUNS is $C_6H_2(OCH_3)_2CN(NO_2)_2$, 1, 2, 3, 4.

At the same time it was shown that the movable NO_2 -group in this substance is placed at 3; consequently we now know the constitution of the compounds obtained from it by substitution of the NO_2 -group by OH , OCH_3 , etc.

Finally, the constitution was determined of the dinitrodimethoxybenzonitrile obtained by the nitration of $C_6H_3(OCH_3)_2CN$ 1, 3, 2, or of the nitrodimethoxybenzonitrile $C_6H_3(OCH_3)_2CN.NO_2$ 1, 3, 2, 4.²⁾ This compound was converted into 4,6-dinitro-resorcine m.p. 215° by being heated for 5 hours at $150^{\circ} - 160^{\circ}$ with hydrochloric acid (30 % HCl); from this follows that its constitution is $C_6H_3(OCH_3)_2CN(NO_2)_2$ 1:3.2.4.6.



4,6 dinitro-2-cyano 1,3 dimethoxybenzene on treatment with alcoholic ammonia or methylamine readily yields compounds which perfectly resemble the compounds which have been obtained in a similar manner from 2,4,6 trinitroresorcinoldimethylether.



¹⁾ LELLMANN and GROTHMANN. Ber. 17, 2731.

²⁾ Dissertation VAN GEUNS. p. 69.