

Citation:

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is also shown by the fact that, the colour having become blue or green on cooling, turns again violet on warming, so long as the solid phase *S* has not yet been attained. The phase is, therefore, realisable at a change of temperature in *two* directions.

§ 7. As I had but very little of the substance at my disposal, the thermometric determinations could only be studied in capillary tubes with the aid of a magnifying glass.

At 82.°1 the phase *S* melts to a doubly-refracting phase *B* which becomes clear at 86.°4 and passes into *L*. On cooling this isotropous fusion, it first passes properly into *B* at 86.°4, but at 84° into the more strongly doubly-refracting phase *A*, which may be undercooled many tens of degrees, and with retention of its violet colour, before passing into the solid phase *S*.

Want of material prevented my determining the true solidifying point of *S* by inoculation; I estimate it at about 80°.

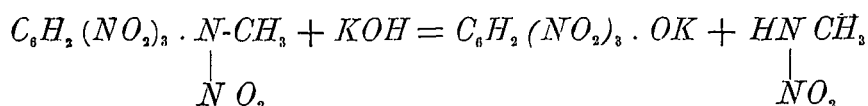
Thus the positive proof has been given that the remarkable colour phenomena accompanying the melting the cholesterol esters *cannot* be attributed to the presence of an ethylene double bond; also that an eventual presence of funaroid and maleinoid isomers cannot be considered as the cause of the occurrence of the *three* liquids.

Zaandam, 15 Febr. 1907.

Chemistry. — “*On the action of bases, ammonia and amines on s. trinitrophenyl-methylnitramine.*” By Prof. P. VAN ROMBURGH and Dr. A. D. MAURENBRECHER.

(Communicated in the meeting of February 23, 1907).

s.-Trinitrophenyl-methylnitramine, as has been known for a long time, is decomposed at the ordinary temperature by ammonia in alcoholic solution, or on warming, by an aqueous solution of potassium hydroxide, or carbonate, in the first case with formation of picramide, in the second (with evolution of monomethylamine) of picric acid. One of us who formerly studied the reaction with bases concluded, from the occurrence of the amine and the formation of nitric acid which was also observed, that the methylnitramine which might be expected according to the equation :



might have become decomposed¹⁾.

From the reaction of methylamine on tetranitrophenyl-methylnitramine and on trinitromethylamidomethylnitramidobenzene he afterwards concluded²⁾ that, probably, there had been formed methylnitramine, meanwhile discovered by FRANCHIMONT and KLOBBE³⁾.

The amount of amine formed by the decomposition of trinitrophenyl-methylnitramine by alkalis is considerably smaller than might be expected from theory; the possibility, therefore, exists that the reaction proceeds indeed mainly in the above indicated sense.

We have, therefore, taken up the problem again in the hope that by suitable modifications in the reaction, we might get at a process for the preparation of methylnitramine which would have the advantage of yielding this costly substance from a cheap, easily accessible material. We were not disappointed in our expectations.

If trinitrophenyl-methylnitramine, which is the final product of the nitration of dimethylaniline and melts at 127°, is boiled with a 10% solution of potassium carbonate a brownish-red solution is obtained, which on cooling gives an abundant deposit of potassium picrate. If after filtration the liquid is acidified with sulphuric acid and again filtered off from the picric acid precipitated and then agitated with ether, the latter yields on evaporation crystals, which after purification, melt at 38°, and are identical with methylnitramine, as was proved by comparing the compound with a specimen kindly presented to us by Prof. FRANCHIMONT. The yield, however, was very small.

If the finely powdered nitramine, m. p. 127°, is treated with 20% methylalcoholic ammonia this becomes intensely red, the mass gets warm and after a few hours the reaction is complete, and a large amount of picramide has formed which is removed by filtration. The alcoholic solution is distilled in vacuo, the residue treated with dilute sulphuric acid and, after removal of a yellowish byproduct by filtration, the liquid is agitated with ether. On evaporation of the ether, crystals of methylnitramine were obtained. In this reaction also, the yield was not large, amounting to only 15% of the theoretical quantity. With ethyl-alcoholic ammonia a similar result was obtained, whereas an experiment in which ammonia was passed into a solution

1) Rec. d. Trav. chim. d. Pays-Bas, II. (1883) p. 115.

2) Ib. VIII (1889) p. 281.

3) Ib. VII (1888) p. 354.

of the nitramine in benzene gave results which were still less favourable.

One of us had noticed previously that among the aromatic amines which generally react on an alcoholic solution of the nitramine quite as readily as on picryl chloride, *p*-toluidine in particular gives a beautifully crystallised *p*-toluylpicramide m. p. 166°¹⁾ whilst the alcoholic solution contains only comparatively few, not very dark coloured byproducts. In an experiment in which 35 grams of the nitramine were heated on the waterbath with an equal weight of *p*-toluidine and 100 c.c. of 96 % alcohol, a fairly violent reaction set in after some time. The heating was continued for 5 hours and, after the picramide derivative had been removed by filtration, the alcohol was distilled off and the residue extracted with dilute sulphuric acid. The liquid filtered off from the toluidine sulphate was shaken with ether. On evaporation of the ether a still yellow coloured liquid product was left which on being inoculated with a crystal of methylnitramine became crystalline and after having stood for some time over sulphuric acid weighed 7 grams. On pressing between filter paper light yellow crystals were obtained which after being sublimed in vacuo (a treatment which methylnitramine stands very well) melted at 38°. On mixing the same with a preparation consisting of pure nitramine the melting point was not affected.

p-Toluidine appears, therefore, to be a suitable means for readily procuring in a short time methylnitramine from *s*-trinitrophenylnitramine.

We are continuing our investigations with different amines and also with other nitrated aromatic nitramines, and will state the results more elaborately in the "Recueil".

Org. Chem. Lab. of the University *Utrecht*.

Physics. — "*Wave-lengths of formerly observed emission and absorption bands in the infra-red spectrum.*" By Prof. W. H. JULIUS.

If in the infra-red spectrum, as formed by means of a rock-salt prism, the positions of emission or absorption bands have been carefully determined, the corresponding wave-lengths still are uncertain by an amount which, in a considerable part of the spectrum, is greater than the probable error of those determinations, because the

¹⁾ We now obtained this substance in two modifications, one coloured dark red and the other orange.