

## On Preparation of 2,4,6-Trinitrophenylacetic Acid

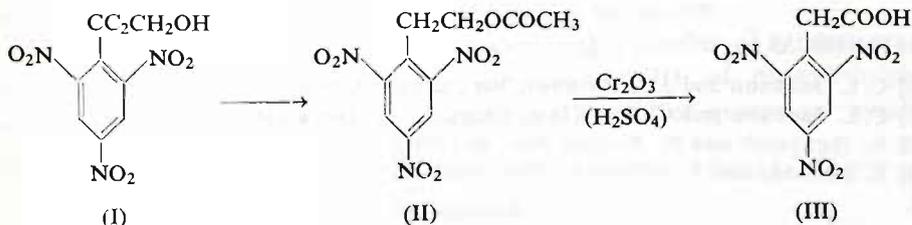
by

Z. BONECKI and T. URBAŃSKI

Presented by T. URBAŃSKI on May 18, 1961

2,4,6-Trinitrophenylacetic acid was obtained by Jackson and Phinney [1] by hydrolyzing diethyl ester of 2,4,6-trinitrophenylmalonic acid. The latter was prepared [2], [3] by reacting picryl chloride with diethyl malonate in presence of sodium ethoxide followed by hydrolysis of the ester and its decarboxylation.

It has now been established that 2,4,6-trinitrophenylacetic acid (III) can be prepared by oxidizing 2,4,6-trinitro- $\beta$ -phenylethanol (I). However, two products were simultaneously obtained: (III) and 2,4,6-trinitrobenzoic acid and the reaction was of little use for preparing pure (III). A much better yield of the product (III) of higher purity was achieved when acetic ester of 2,4,6-trinitro- $\beta$ -phenylethanol (II) was oxidized. The oxidation was carried out by chromic acid in solution of sulphuric acid.



### Experimental

2,4,6-Trinitro- $\beta$ -phenylethanol (I) was prepared as previously described [4].

#### 2,4,6-Trinitro- $\beta$ -phenylethyl acetate (II)

The ester (II) was prepared in two ways: (a) and (b).

(a) 2,4,6-Trinitrophenylethanol (I) (10 gm.) was dissolved in acetic anhydride (25 ml.) and the solution was refluxed for two hours. The excess of acetic anhydride was then distilled off and the concentrated solution was poured into water. The crystalline product (II) was collected and crystallized from benzene or glacial acetic acid.

The yield was 9 gm., m.p. 98°C.

(b) (I) (10gm.) was dissolved in benzene to obtain a saturated solution. Acetyl chloride, 50 per cent solution in benzene, was added dropwise on stirring at room temperature. Subsequently acetyl chloride was introduced, the solution was mixed for *c.* 15 min. and then concentrated under reduced

pressure to *c.* 1/3 of its original volume. Ester (II) crystallized on cooling. The yield was 10 gm., m.p. 98°C.

Ester (II) is soluble in benzene, ethanol, acetone and acetic acid.

Analysis:

$C_{10}H_9O_8N_3$  requires 40.0% C, 3.3% H, 14.0% N,  
found 40.0% C, 3.3% H, 14.2% N.

#### 2,4,6-Trinitroacetic acid (III)

2,4,6-Trinitrophenylethylacetate (II) (10 gm.) was dissolved in sulphuric acid (*d* — 1.84) (100 gm.). Powdered chromium trioxide (10 gm.) was added to the solution. The temperature was maintained below 30°C by cooling. The colour of the liquor turned gradually green. After three quarters of chromium trioxide had been introduced, the temperature was gradually increased to 45°C by less intensive cooling. Intensive gas evolution and foaming accompanied the reaction. When all the chromium trioxide had been introduced, the reaction liquor was stirred for 3—3.5 hours at 45°C. Then the temperature was carefully increased to 80—85°C. If foaming was excessive, a few milliliters of sulphuric acid were added.

The temperature was eventually brought to 90°C and maintained so for 30 min. The reaction was considered as ended when no more gas evolved and foaming ceased.

After cooling the reaction liquor was poured into ice and the precipitated product (III) collected. It was washed with water to remove  $Cr^{3+}$  and  $SO_4^{2-}$  ions and was crystallized from benzene or acetic acid.

The yield was 7 gm. (77%), m.p. 163—165°C.

The acid (III) is of lemon-yellow colour, soluble in benzene, toluene, ethanol and acetic acid.

Analysis:

$C_8H_5O_8N_3$  requires 35.4% C, 1.8% H, 15.5% N,  
found 35.2% C, 2.0% H, 15.75% N.

MILITARY TECHNICAL COLLEGE, WARSAW  
(WOJSKOWA AKADEMIA TECHNICZNA, WARSZAWA)

#### REFERENCES

- [1] C. L. Jackson and J. J. Phinney, *Ber.*, **28** (1895), 3067.
- [2] C. L. Jackson and C. Soch, *Am. Chem. J.*, **18** (1896), 134.
- [3] A. Hantzsch and N. Picton, *Ber.*, **42** (1909), 2126.
- [4] Z. Bonecki and T. Urbański, *Bull. Acad. Pol. Sci., Sér. sci. chim.*, **9** (1961), 463 [this issue].