

ACTION OF *p*-TOLUENE-SULPHONYL CHLORIDE ON NITROPHENOLS

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The action of *p*-toluene-sulphonyl chloride on ethyl 2-oxy-3 : 5-dinitro-1-benzoate and ethyl 4-oxy-3 : 5-dinitro-1-benzoate has been examined. In both the cases the OH group is replaced by chlorine, in the presence of diethylaniline as the condensing reagent.

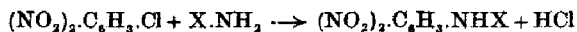
These chloro compounds have been found to be identical with the dinitrochlorobenzoic esters obtained by nitrating *o*- and *p*-chlorobenzoic acids respectively and subsequent esterification.

The action of various amines and amino compounds on these chloro compounds has also been studied.

It has been observed by Ullmann and his collaborators (Ullmann and Nadai, *Ber.*, 1908, 41, 1870 ; Ullmann and Bruick, *Ber.*, 1908, 43, 3939-3932 ; Ullmann and Sane, *Ber.*, 1911, 44, 37 ; Sane and Joshi, *J. Chem. Soc.*, 1924, 2481 ; *J. Indian Chem. Soc.*, 1928, 5, 299 ; Sane, Chakravarty and Pramanick, *ibid.*, 1932, 9, 55 ; Sane and Joshi, *ibid.*, 1932,

9, 59; 1933, 10, 459; Joshi, *ibid.*, 1933, 10, 313) that *p*-toluene-sulphonyl chloride reacts with nitrophenols in two ways, mononitrophenols form *p*-toluene-sulphon esters either in the presence of sodium carbonate or diethylaniline as the condensing reagent; poly-nitrophenols, specially containing NO₂ groups in the 2: 4 or 2:6 position to the OH group, also yield such esters in the presence of sodium carbonate as the condensing agent, but in the presence of diethylaniline they are mainly converted into poly-nitrochlorobenzenes, the OH group being replaced by Cl.

The chloro compounds obtained from these poly-nitrophenols are usually extremely reactive. In alcoholic, benzene or toluene solution, they react with a number of amines, yielding as a rule substituted nitroamines.



In the present paper, the above reaction has been extended to ethyl 2-oxy-3:5-dinitro-1-benzoate and ethyl 4-oxy-3:5-dinitro-1-benzoate and in both the cases chloro compounds have been obtained. The chloro compounds so obtained are found to be extremely reactive, as the presence of two nitro groups, specially in the *ortho* and *para* position of the halogen atom, makes it extremely labile. They have been reacted with a number of amines and the compounds so formed are isolated and characterised.

EXPERIMENTAL

Ethyl 3:5-dinitro-2-oxy-1-benzoate has been obtained either by nitrating salicylic acid and then esterifying (Cahour, *Annalen*, 1849, 69, 235) or by the direct nitration of ethyl salicylate (*Annalen*, 1850, 74, 313). The exact details of the second method are, however, not available in the literature. It has therefore been prepared by us in the following manner.

A solution of ethyl salicylate (25 c.c.) in glacial acetic acid (25 c.c.) was added during the course of 1 hour through a tap funnel to a mixture of fuming nitric acid (70 c.c.) and concentrated sulphuric acid (30 c.c.), which was cooled by a current of water. It was then allowed to stand for 24 hours and then heated finally over a wire-gauze for 5 minutes. After cooling, this mixture was poured into about 600 c.c. of water when the nitro compound separated out as a white crystalline powder. This was filtered and washed thoroughly with water, yield of the crude product (m.p. 96°) is about 37 g. On recrystallising from alcohol the m.p. rose to 98°.

Ethyl 3:5-Dinitro-2-chloro-1-benzoate.—Ethyl 3:5-dinitrosalicylate (5 g.), *p*-toluene-sulphonyl chloride (4 g.) and diethylaniline (10 c.c.) were heated together in a flask over a water-bath for 4 hours. The mixture was then cooled and an excess of hydrochloric acid added to it. The semi-solid mass, which now separated out, was washed with water and then with a dilute solution of sodium carbonate and then again with water. The substance, which now solidified, was filtered and then recrystallised from alcohol, m.p. 54°.

This substance was found to be identical with the chlorobenzoic ester, which was obtained by the nitration of *o*-chlorobenzoic acid and subsequent esterification (Cohn,

Monatsh, 1901, 22, 388) and the corresponding amino compounds obtained from these two substances separately by the action of various amines were also found to be identical.

Ethyl 3 : 5-dinitro-4-oxy-1-benzoate was obtained by the esterification of 3 : 5-dinitro-4-oxybenzoic acid according to the method of Salkowski (*Annalen*, 1872, 163, 44).

Ethyl 3 : 5-Dinitro-4-chloro-1-benzoate.—Ethyl 3 : 5-dinitro-4-oxy-1-benzoate (2.5 g.), *p*-toluene-sulphonyl-chloride (2 g.) and diethylaniline (5 c.c.) were heated together in a flask over a water-bath for 4 hours. It was then cooled and digested with hydrochloric acid. The chloro compound was then isolated in the usual way and finally recrystallised from alcohol, m.p. 82°.

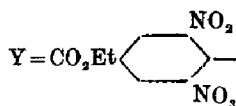
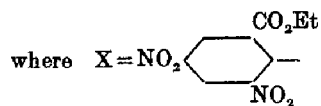
This substance was also found to be identical with the chlorodinitrobenzoic ester, which was obtained by the nitration of *para*-chlorobenzoic acid and esterification (Ullmann *Annalen*, 1908, 366, 93), and the corresponding amino compounds obtained from these substances separately by the action of various amines were also found to be identical.

Reaction with Amines.—The calculated quantities of the chloro compound and the appropriate amine (slight excess) were dissolved separately in alcohol and then mixed and refluxed for 1 hour. The alcohol was then distilled off and the excess of amine removed by the addition of concentrated hydrochloric acid. The solid which now separated out was washed with boiling water and then recrystallised from a suitable solvent.

The various amino compounds obtained by the action of a number of amines on these two chlorodinitrobenzoic esters have been given in Table I

TABLE I

| Reactants. | Formulae. | M.p. | Colour. | Nitrogen | |
|---|---|------|-----------------|----------|--------|
| | | | | Found. | Calc. |
| Ethyl 3 : 5-dinitro-2-chloro-1-benzoate | Aniline X.NH.C ₆ H ₅ | 140° | Yellow | 12.30% | 12.70% |
| „ | <i>o</i> -Toluidine X.NH.C ₆ H ₄ .CH ₃ | 119° | Yellow | 11.80 | 12.17 |
| „ | <i>m</i> -Toluidine X.NH.C ₆ H ₄ .CH ₃ | 132° | Yellow | 11.60 | 12.17 |
| „ | Piperidine X.N.C ₅ H ₁₀ | 109° | Lemon-yellow | 12.75 | 13.00 |
| „ | <i>o</i> -Amino-phenol X.NH.C ₆ H ₄ .OH | 150° | Chocolate-brown | 11.70 | 12.09 |
| „ | <i>o</i> -Anisidine X.NH.C ₆ H ₄ .OCH ₃ | 163° | Scarlet-red | 11.30 | 11.66 |
| Ethyl 3 : 5 dinitro 4-chloro-1-benzoate | Aniline Y.NH.C ₆ H ₅ | 163° | Orange-yellow | 12.50 | 12.76 |
| „ | <i>o</i> -Toluidine Y.NH.C ₆ H ₄ .CH ₃ | 151° | Turmeric yellow | 11.90 | 12.17 |
| „ | <i>m</i> -Toluidine Y.NH.C ₆ H ₄ .CH ₃ | 141° | Orange | 12.10 | 12.17 |
| „ | Piperidine Y.N.C ₅ H ₁₀ | 90° | Yellow | 12.70 | 13.00 |
| „ | <i>o</i> -Amino-phenol Y.NH.C ₆ H ₄ .OH | 168° | Orange | 12.40 | 12.09 |
| „ | <i>o</i> -Anisidine Y.NH.C ₆ H ₄ .OCH ₃ | 163° | Red | 11.65 | 11.66 |



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