

### 63. The Preparation of Symmetrical Dinitrodiphenyls by the Ullmann Reaction.

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Symmetrical dinitrodiphenyls have been prepared by the Ullmann reaction, under standard reaction conditions, from pure halogenonitrobenzenes. The results obtained enable a valid comparison of the reactivities of the halogen atoms to be made. The *o*-nitro-group has a greater activating effect on halogen atoms than *p*- or *m*- nitro-groups.

In a recent comprehensive review of the Ullmann reaction (Fanta, *Chem. Reviews*, 1946, **38**, 139), the reaction conditions for the preparation of symmetrical dinitrodiphenyls and the yields obtained by various workers are incomplete and hence no valid comparison of the reactivities of the halogen atoms in the halogenonitrobenzenes is possible. In the present work standard conditions have been used for the preparation of symmetrical dinitrodiphenyls, and the results therefore enable a true comparison of the reactivities to be made.

Carefully purified halogenonitro-compounds have been converted into diaryls by heating them with freshly precipitated copper in the dry state, and by heating their solutions in nitrobenzene with freshly precipitated copper. In general, the fusion method has given a smoother reaction and a higher yield of the diaryl than the reaction in solution. The results confirm those of previous workers and show that iodo-compounds give the highest yields and the purest products. The activating effect of the nitro-group on halogen atoms is in the order ortho > para > meta, and this is in general agreement with the conclusions of Fanta (*loc. cit.*) for the Ullmann reaction.

#### EXPERIMENTAL.

(All m. ps. are uncorrected.)

*Starting Materials.*—Nitroanilines were converted into chloronitro-, bromonitro-, and iodonitro-compounds by the Sandmeyer reaction or by treatment of the diazonium solution with potassium iodide. The crude halogenonitro-compounds were twice distilled in steam, twice crystallised from alcohol, and then dried for several days over phosphoric oxide in a vacuum. Although these compounds distil very slowly in steam, this method has been found the most satisfactory for their purification.

Pure nitrobenzene was prepared by drying A.R. nitrobenzene over potassium hydroxide and then twice distilling it, rejecting the first and the last 20% of the distillate.

Freshly precipitated copper was prepared by gradual addition of A.R. zinc dust to excess of an aqueous solution of A.R. copper sulphate just acidified with sulphuric acid. The precipitate was collected, thoroughly washed with distilled water, alcohol, and finally ether, and dried in a vacuum. The copper was freshly precipitated for each series of reactions, standard conditions being used for the preparation.

*Ullmann Reaction by Fusion.*—The halogenonitrobenzene (2.5 g.) was placed in a previously dried test tube, embedded in a sand-bath and fitted with a thermometer. The bath was heated to 200° as indicated by the thermometer, and copper powder (1.5 g.) was added in small portions over a period of 20 minutes, the whole being constantly stirred by means of the thermometer. When all the copper powder had been added the temperature was maintained at 200° for a further 10 minutes, raised to 220° and maintained at this temperature for a final 10 minutes, stirring being continued throughout.

After cooling, the tube and contents were crushed and extracted in a Soxhlet apparatus with benzene, care being taken to avoid loss of material during extraction. The bulk of the benzene was removed by distillation, and the remaining benzene and unchanged nitrohalogen compound were removed by exhaustive distillation in steam. The residue was filtered and extracted with hot alcohol. The alcoholic solution was then evaporated to dryness in a wide-mouthed flask on a steam-bath. Alcohol, saturated at 0° with the appropriate dinitrodiphenyl, was then added, and the contents of the flask were heated under reflux until solution was complete. The flask was then cooled and maintained at 0° for 1 hour

The crystals which separated were collected rapidly in a pre-cooled funnel, and after being washed with a little saturated alcoholic solution were cooled to 0°, dried in vacuum over phosphoric oxide, and weighed.

When no crystals separated from the alcoholic solution after 1 hour at 0°, the flask was maintained at 0° for a further 30 minutes before the yield was reported as nil.

*Ullmann Reaction in Nitrobenzene Solution.*—The halogenonitrobenzene (5 g.) was added to copper powder (3 g.) and nitrobenzene (25 g.), and the whole refluxed for 9 hours. After cooling, the contents of the flask were diluted with a little dry benzene and filtered, and the residue was well washed with warm benzene. The benzene–nitrobenzene solution was then exhaustively distilled in steam to remove benzene, nitrobenzene, and unchanged halogenonitro-compound. The residue, after filtration, was dissolved in alcohol and purified as before.

All experiments were carried out in duplicate and repeated using copper-bronze. No marked improvement in yield was obtained by the use of copper-bronze.

The results are summarised in the table together with the reported yields obtained by other workers.

*Comparative yields of dinitrodiphenyls.*

Nitrohalogen compound.	Yield by fusion (%).	Yield by reaction in nitrobenzene (%).	Yields reported by other workers.	Ref. No.
<i>o</i> -Chloronitrobenzene	40	Nil	52—61 52—54 (occasionally 61)	(1) (3)
<i>o</i> -Bromonitrobenzene	64	45	60 75	(2) (2)
<i>o</i> -Iodonitrobenzene	65	43	—	(4)
<i>m</i> -Chloronitrobenzene	Nil	Nil	—	—
<i>m</i> -Bromonitrobenzene	15	Nil	—	(4)
<i>m</i> -Iodonitrobenzene	36	Nil	26—52	(5), (6)
<i>p</i> -Chloronitrobenzene	Nil	Nil	—	—
<i>p</i> -Bromonitrobenzene	36	15	—	(7)
<i>p</i> -Iodonitrobenzene	54	25	52	(8)

The references in the last column are used in the discussion which follows.

DISCUSSION.

The yields of *o*-halogenonitro-compounds obtained by the fusion method are somewhat lower than those reported by Fuson and Cleveland (1) (*Org. Synth.*, 1940, 20, 45), Ullmann (2) (*Ber.*, 1901, 34, 2174), and Shaw and Turner (3) (*J.*, 1933, 135), but these authors used higher reaction temperatures. The preparation of 2 : 2'-dinitrodiphenyl by this reaction has also been described by Le Fèvre (*J.*, 1929, 733; 1938, 967), Schiemann and Rozelius (4) (*Ber.*, 1932, 65, 737), and Mascarelli, Longo, and Ravero (*Gazzetta*, 1938, 68, 33), but none of these workers give any indication of the yield. In the attempted preparation of 2 : 2'-dinitrodiphenyl in nitrobenzene solution a small amount of purple material was produced, but no diphenyl could be isolated, even by chromatographic separation on alumina.

The yields of *m*-halogenonitrobenzenes are in agreement with those obtained by Cumming and Muir (5) (*J. Roy. Tech. Coll., Glasgow*, 1937, 4, 61). Mascarelli, Longo, and Ravero (6) (*loc. cit.*), Schiemann and Rozelius (*loc. cit.*), and Ullmann and Bielecki (*loc. cit.*) have all described the preparation of 3 : 3'-dinitrodiphenyl but have given no indication of yield.

The yields of 4 : 4'-dinitrodiphenyl agree with those obtained by Ullmann and Bielecki (*loc. cit.*). Mascarelli, Longo, and Ravero (*loc. cit.*) described the preparation of this compound, but gave no indication of the yield.

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