

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF MCMASTER UNIVERSITY.]

## FRIEDEL AND CRAFTS' REACTION. DIPHENYL AND DITOLYL TETRAHALOGEN PHTHALIDES.

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This work was undertaken in order to study the diphenyl and ditolyl tetrahalogen phthalides, and to investigate the applicability of the method proposed by Rubidge and Qua<sup>1</sup> for the preparation of diphenyl-phthalide.

These authors heated phthalic anhydride, benzene and aluminum chloride together until hydrogen chloride was no longer evolved. An acid anhydride was then added and the heating continued for about 3 hours. The acid anhydride reacts with the intermediate compound formed and diphenyl phthalide is the final product. Of the acid anhydrides used, acetic anhydride was found to give the best results. This method was used in the experiments described below.

In the reactions described in this paper tetrabromo- and tetra-iodo-phthalic anhydrides were used with aluminum chloride and either benzene or toluene. In most cases good yields of the phthalides were obtained.

The diphenyl- and ditolyl-tetrachloro-phthalides have been prepared by Orndorff and Murray<sup>2</sup> who obtained them by treating tetrachloro-phthalyl chloride with benzene and toluene respectively. We prepared these two compounds by Rubidge's method and found them identical with Orndorff's products.<sup>3</sup>

**Tetrabromo-phthalic Anhydride with Aluminum Chloride and Benzene.**—Ten g. of anhydride was shaken up with 45 cc. of benzene and then 6.3 g. of aluminum chloride was slowly added. All the hydrogen chloride had been evolved after the mixture had stood for 9 hours on the water-bath at 80°. Seven cc. of acetic anhydride was added and the reaction was allowed to stand for 3 hours longer at the same temperature. Fifty cc. of 10% hydrochloric acid was then added and the excess of benzene was removed by distillation with steam; yield, 94%. The product was recrystallized from glacial acetic acid and melted at 202°. It is soluble in benzene, toluene and chloroform, slightly soluble in ethyl alcohol and insoluble in ligroin and water. This compound was found to be diphenyl-tetrabromo-phthalide.

*Analysis.* Calc.: Br, 53.16. Found: 53.5.

**Tetrabromo-phthalic Anhydride with Aluminum Chloride and Toluene.**—Ten g. of anhydride, 45 cc. of toluene, 6.3 g. of aluminum chloride and 7 cc. of acetic anhydride were used and the reaction carried out as above, except at 96–98°; yield, 93%. Recrystallized from glacial acetic acid, the product melted at 196–197°. It is soluble in benzene, toluene and chloroform, slightly soluble in ether and alcohol and insoluble in

<sup>1</sup> Rubidge and Qua, *THIS JOURNAL*, **36**, 732 (1914).

<sup>2</sup> Orndorff and Murray, *ibid.*, **39**, 294 (1917).

<sup>3</sup> The melting point of diphenyl-tetrachloro-phthalide is stated by Orndorff and Murray to be 250°; our product melted at 150°, and on second recrystallization at 151°. In a private communication Dr. Orndorff states that a typographical error occurred in their paper and that the melting point should have been given as 150°.

water. Method of preparation and analytical results show this substance to be ditolyl-tetrabromo-phthalide.

*Analysis.* Calc.: Br, 50.83. Found: 51.08.

**Tetra-iodo-phthalic Anhydride with Aluminum Chloride and Benzene.**—Ten g. of anhydride, 40 cc. of benzene, 4.4 g. of aluminum chloride and 6 cc. of acetic anhydride were taken, the temperature of reaction being about 80°. The phthalide obtained is soluble in benzene, toluene and chloroform, slightly soluble in ether, ligroin and ethyl alcohol, and insoluble in water. When recrystallized from glacial acetic acid it melted at 206°; yield, 61%. It has a very pale yellow color. This compound was shown to be diphenyl-tetra-iodo-phthalide.

*Analysis.* Calc.: I, 64.33. Found: 64.01.

**Tetra-iodo-phthalic Anhydride with Aluminum Chloride and Toluene.**—The reaction was carried out as above at 97–98° with 10 g. of anhydride, 40 cc. of toluene, 4.4 g. of aluminum chloride, and 6 cc. of acetic anhydride. The product was treated with small quantities of cold acetone to remove the tar formed during the reaction. The residue was recrystallized from glacial acetic acid and melted at 213–214°; yield, 42%. It is soluble in benzene and chloroform, and slightly soluble in ethyl and methyl alcohols ether and ligroin. Our purest product had a pale yellow color. The synthesis and analysis show this substance to be ditolyl-tetra-iodo-phthalide.

*Analysis.* Calc.: I, 62.1. Found: 62.5.

### Summary.

1. The method used by Rubidge and Qua for the preparation of diphenyl phthalide was found to give good results in the preparation of the diphenyl and ditolyl tetrahalogen phthalides.
2. Four new substituted phthalides have been prepared and their properties described: diphenyl-tetrabromo-phthalide, m. p. 202°; ditolyl-tetrabromo-phthalide, m. p. 196–197°; diphenyl-tetra-iodo-phthalide, m. p. 206°; ditolyl-tetra-iodo-phthalide, m. p. 213–214°.

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## THE REARRANGEMENT OF BENZIL TO BENZILIC ACID.

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The mechanism whereby benzil, under the influence of alkalis, is converted into benzilic acid has long been a matter of speculation. Four different hypotheses have occupied the attention of recent investigators. Nef<sup>1</sup> assumed an addition of water to benzil, followed by dissociation into benzophenone and "dioxymethylene;" the latter substance, after changing over into formic acid, was then supposed to condense with the former by carbonyl condensation, thus yielding benzilic acid. Schroeter<sup>2</sup> postulated the intermediate formation of diphenylketene. This view, however, has been tested experimentally by Nicolet and Pelc,<sup>3</sup> and found untenable. Tiffeneau, recognizing the analogy between the benzil rearrangement

<sup>1</sup> Nef, *Ann.*, **298**, 372 (1897).

<sup>2</sup> Schroeter, *Ber.*, **42**, 2336 (1909).

<sup>3</sup> Nicolet and Pelc, *THIS JOURNAL*, **43**, 935 (1921).