

KURZE MITTEILUNGEN

Bis am 20. des Monats bei der Redaktion eingehende kurze Mitteilungen werden in der Regel am 15. des folgenden Monats veröffentlicht
Es werden auch Manuskripte aus dem Auslande angenommen

Halogenobenzaldehydes

Part IV*

Zusammenfassung

Die Methode, die BEECH für die Überführung primärer aromatischer Amine in die zugehörigen Aldehyde entwickelt hat und die von uns auf Halogenaniline ausgedehnt wurde, wird in ihrer Anwendung zur glatten Synthese einiger Halogenbenzaldehyde beschrieben.

It has been reported earlier by us¹ that halogenobenzaldehydes can be conveniently prepared from the corresponding halogen substituted anilines by adopting the reaction due to BEECH,² viz. interaction of the diazonium salt of the amine with formaldoxime followed by hydrolysis. 2-methyl-5-chlorobenzaldehyde and 2-methyl-5-bromobenzaldehyde were required in connection with the preparation of 4-methyl-7-chloro- and 4-methyl-7-bromohydrindone needed for other work in progress in these laboratories. These two aldehydes have now been prepared for the first time starting with the appropriate aniline and subjecting them to the Beech reaction outlined above.

It may be pointed out that the easy availability of these aldehydes by the above synthesis and their facile conversion into the corresponding hydrocinnamic acid through Knoevenagel reaction and subsequent reduction constitute a convenient route for the unambiguous synthesis of the appropriate hydrindones.³

On the contrary the methods adopted by FIESER and SELIGMAN⁴ for the preparation of such hydrindones e.g. 4-chloro-7-methylhydrindone involves a wasteful process of separation by fractional distillation of this compound from the isomeric 4-methyl-7-chlorohydrindone simultaneously formed besides loss in yield due to the formation of biindanones during such distillation.

* Received April 30, 1962.

¹ S.D. JOLAD and S. RAJAGOPAL, *J. Sci. Ind. Res. (India)* 21B (1961) 359; id., *Naturwiss.* 48 (1961) 645. N. GUDI, S. HIREMATH, V. BADIGER and S. RAJAGOPAL, *Arch. Pharm.* 295 (1962) 16. S. D. JOLAD, S. S. VERNEKAR and S. RAJAGOPAL, *Mh. Chem.* 93 (1962) 271.

² W. F. BEECH, *J. Chem. Soc.* 1954, 1297.

³ S. D. JOLAD and S. RAJAGOPAL, under publication.

⁴ L. F. FIESER and A. M. SELIGMAN, *J. Amer. Chem. Soc.* 57 (1935) 942, 58 (1936) 2482.

The aldehydes now prepared have been characterised by the preparation of 2,4-dinitrophenylhydrazones and the corresponding cinnamic acids.

Experimental

2-Methyl-5-chlorobenzaldehyde: Ten per cent solution of formaldoxime for use in conjunction with the diazonium salt (0.25 mole) was made by heating paraformaldehyde (11.5 g) with hydroxylamine hydrochloride (26.3 g in 170 ml water) until a clear solution was obtained. Sodium acetate (51 g) was added and the mixture boiled gently under reflux for 15 minutes.

In the meanwhile a solution of 2-methyl-5-chloro benzene diazonium chloride was prepared from 2-methyl-5-chloroaniline⁵ (36.0 g, 0.25 mole) at 0 to 5°C and employing concentrated hydrochloric acid (57 ml), water (50 ml), ice (100 g) and a solution of sodium nitrite (17.5 g in 25 ml water). This was made neutral to congo-red by the addition of hydrated sodium acetate (22 g) in water (35 ml). The neutral diazonium-chloride solution was then introduced below the surface of 10 per cent aqueous formaldoxime to which had been added copper sulphate (6.25 g), sodium sulphite (1 g) and hydrated sodium acetate (160 g) in water (180 ml) at 10 to 15° with vigorous stirring. Stirring was then continued for another hour. The mixture was then rendered acidic to congo-red and after addition of more acid (230 ml) it was boiled under reflux for 2 hrs. and subjected to steam distillation. The distillate was neutralised with sodium bicarbonate and extracted with ether.

The crude product obtained by distilling off ether was shaken with aqueous sodium metabisulphite (90 ml, 40%) at 60°. The addition product was filtered and washed twice with ether to remove any non-aldehydic material. After regeneration from aqueous layer by boiling with aqueous sulphuric acid the aldehyde was extracted with ether. The ether extract was dried over anhydrous magnesium sulphate. When distilled under reduced pressure 2-methyl-5-chlorobenzaldehyde was obtained as a colourless oil, b.p. 103 to 104°/8 mm; n_D^{25} 1.562; yield: 46% [found: Cl, 22.42, C₈H₇ClO requires Cl, 22.98%]. The 2,4-dinitrophenylhydrazone crystallised from acetic acid as orange needles, m.p. 246 to 247°.

The cinnamic acid prepared by heating the above aldehyde (0.5 g), malonic acid (0.5 g), pyridine (1 ml) and piperidine (1 drop) under reflux crystallised from aq. alcohol as colourless shining needles, m.p. 185° [found: C 60.83, H 4.26, C₁₀H₉O₂Cl (196.5); requires C 61.06, H 4.58; equivalent weight: found 198, calc. 196.5].

⁵ H. GOLDSCHMIDT and M. HÖNIG, *Ber. deutsch. chem. Ges.* 19 (1886) 2438.

2-Methyl-5-bromobenzaldehyde was prepared from 2-methyl-5-bromoaniline⁶ following the same procedure as described above for the other aldehyde. It was obtained as a colourless oil, b.p. 171 to 172°/85 mm; m.p. 43.5°; yield 41% (found: Br 39.5, C₈H₇BrO requires Br 40.2%).

The 2,4-dinitrophenylhydrazone was obtained as red shining needles, m.p. 253°.

⁶ N. W. JANNEY, *Liebig's Ann. Chem.* 398 (1913) 354.

The corresponding cinnamic acid melted at 173 to 174° [found: C 49.57, H 3.36; C₁₀H₉O₂Br (241.0) requires C 49.79, H 3.74; equivalent weight: found 239, calc. 241].

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