phenylhydrazone residue was directly replaced by the oxime group, giving the simple oxime of acetonaphthol as a product. As pointed out by Friedländer,[1] it is extremely difficult to obtain the methyl ether of the original compound, acetonaphthol, and it is probable that the protecting influence of the two ortho substituents prevented the substitutions desired.

Reaction with Ferric Chloride.—The majority of phenols in aqueous solution upon the addition of ferric chloride give a characteristic color reaction, and this is almost universal in the case of ortho derivatives.[2] Salicylaldehyde and 5-bromosalicylaldehyde give an intense violet color, and acetonaphthol and bromacetonaphthol give a deep green test. But the phenylhydrazones of the same compounds, in alcoholic solution, give only a faint yellow test; however, the solutions of the alkali-insoluble phenols on standing for a half hour or more, gradually change to a deep red-brown. The same change is brought about more quickly by heating the solution. The phenylhydrazone of salicylaldehyde does not give a color test with ferric chloride even after long standing.

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ON THE MAXIMUM YIELD OF AMINES BY THE REDUCTION OF ALKYL CYANIDES.

BY JITENDRA NATH RAKSHIT.

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Mendius[3] prepared alkylamines by the reduction of their cyanides with zinc dust and dilute hydrochloric acid. Siersch[4] modified the method by arranging a series of vertical tubes filled with granulated zinc, through which a mixture of nitrile, hydrochloric acid, and alcohol had to circulate. The principles involved in the improvement are the exposition of a larger surface in a shorter duration and prevention of hydrolysis by using an alcoholic medium for the reaction. It was further modified by Ladenburg,[5] who introduced alcohol and sodium for the hydrogenation.

Having had to prepare amines in quantities from the nitriles,[6] Mendius', Siersch's and Ladenburg's methods have been successively tried but the bases produced have been always found to be considerably contaminated with ammonia. By the former two only nominal quantities of amines were obtained and by the latter some amines were produced. The yield was much below the theoretical. It had been observed that on increas-

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[1] *Ber.*, 28, 1949 (1895).

[2] Wegscheider and Bittner, *Monatsh.*, 21, 650 (1900).

[3] *Ann.*, 121, 229.

[4] *Ibid.*, 144, 139.

[5] *Ber.*, 19, 1783.

[6] Ray and Rakshit, *Trans. Chem. Soc.*, 99, 1471; 101, 141.

ing the dilution of the nitriles in alcohol the yield of the amine improved. And it had been calculated that the quantity of the nitrogen of ammonia and amine together does not account for the total nitrogen of the cyanide used. This is evidently due to the partial direct action of the nitriles with sodium.[1] E. V. Mayer[2] has shown that sodium acts on ethyl cyanide according to the following equations:

$$2Na + 2EtCN = NaCN + C_2H_6 + C_2H_4NaCN;$$

$$C_2H_4NaCN + C_2H_4CN = C_6H_9NaN_2.$$

The greater the concentration of the cyanide the more of it is acted on by the sodium. On increasing the dilution the formation of sodium cyanide becomes less and less, as is observed by the decreasing amount of Prussian blue obtainable from the resulting sodium ethoxide of the reduction. After a certain dilution its formation and that of ammonia becomes practically nil. The generation of ammonia in this case cannot be ascribed to the hydrolysis of the nitrile because there is no water present and if the ethyl hydroxide be taken for the water and the hydrolysis be assumed, still ammonia cannot result, but either a primary or a secondary base will be formed. It can, however, be explained by assuming the excessive hydrogenation of the nitrile:

$$RCN + 6H = RCH_3 + NH_3.$$

After several experiments it has been found that the following method is most suitable for the maximum yield: Five cc. of the nitrile are diluted with 75 cc. of absolute alcohol. Five grams of freshly cut sodium are introduced into a 500 cc. flask fitted with an inclined reflux condenser and a tap funnel. The mixture is added in portions of 5 cc. at a time and the flask is heated by means of a liquid paraffin bath at temperatures between 50° and 60°. After four such additions 5 cc. of absolute alcohol are to be added and the amine evolved by distillation is absorbed in hydrochloric acid diluted with an equal bulk of water. When all of the mixture has been added, sufficient alcohol is next poured in so that a layer remains above the surface of the solid sodium ethoxide in the flask. When the evolution of hydrogen practically ceases some more alcohol is added and the flask is heated up to the neck on a water bath, taking off the condenser and directly connecting the flask with the absorbing bottles containing acid. Heating is continued as long as any alkaline vapor comes off. If all the alcohol is distilled and yet some amine remains in the flask, more alcohol is to be added and distilled. By evaporating the acid solution on a water bath the crude amine hydrochloride is obtained, which is then extracted with a mixture of 15 cc. of absolute alcohol and 10 cc. water free ether. Thus pure amine hydrochloride is obtained, free from any ammonium chloride, as salammoniac is insoluble

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[1] Frankland and Kolbe, *Ann.*, 65, 281.

[2] *Chem. Soc. Abs.*, 1889, 114.

in the above menstruum, especially when the amine hydrochloride is present in excess.[1] Some typical results are given below:

	Quantity of nitrile. Cc.	Quantity of alcohol. Cc.	Amine hydrochloride. Gm.	Ammonium chloride. Gm.	Theoretical amine hydrochloride. Gm.
Methyl cyanide....	5	50	3.8	0.63	7.9
	5	75	7.6	0.0	7.9
	5	100	7.58	0.0	7.9
Ethyl cyanide.....	5	50	4.36	0.5	7.0
	5	75	6.4	0.07	7.0
Propyl cyanide....	5	75	6.1	0.03	6.3
	5	100	6.0	0.06	6.3

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THIOPHENE ANALOGS OF TRIPHENYLETHYL.

[PRELIMINARY NOTE.]

BY M. GOMBERG AND R. L. JICKLING.

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Thus far the discussion of the triphenylmethyl question has been limited to the study of compounds containing phenyl groups or some of its many homologs. We have now endeavored to extend our study of this subject into compounds of the hetereocyclic series and have attempted to prepare analogs of triphenylmethyl containing other than exclusively aromatic groups.

By means of the Grignard synthesis, thienyldiphenyl carbinol (m. p. 128°) has been prepared from α-iodothiophene and benzophenone.[2] Treating the carbinol with hydrogen chloride gives the chloride, melting at 81°. Analysis: calculated Cl, 12.41%; found Cl, 12.40%. The chloride as first obtained is colorless but becomes more or less colored upon exposure, being in this respect much more sensitive than triphenylmethyl chloride. A benzene solution of the chloride assumes at once a deep red color, when treated with molecular silver or other metals. That the hydrocarbon thus formed is unsaturated in character, has been shown by its absorption of oxygen. By shaking the chloride in nitrobenzene with molecular silver, sealed in the presence of air, the absorption was found to be 5.48%, calculated 5.60%. Similar experiments with benzene as solvent gave 5.98% and 6.07% absorption of oxygen. By shaking the chloride in benzene with silver out of presence of air and afterward exposing to air the hydrocarbon thus formed, the rate of absorption of oxygen has been found to be much lower than that of triphenylmethyl, the amount of absorption finally reaching, however, about three-fourths the theoretical. In this respect the thienyl compound resembles diphenylenephenyl methyl.[3]

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[1] Winkler, *Ann.*, 93, 324; Ray and Rakshit, *J. Chem. Soc.*, 99, 1471.

[2] *Bull. de soc. chim.*, 5,734 (1909).

[3] *Ber.*, 39, 2969 (1906).