

depending upon the amount of cobalt present. If cobalt be absent, the precipitate will be a pale green, and will remain so upon standing.

It will, therefore, be evident that by this test, which is practically instantaneous and requires no manipulation, it is possible in one operation, carried on in a test-tube, to detect both elements, even if either element be in exceedingly small amount, in a great excess of the other, the test for cobalt being probably as delicate as any hitherto proposed (with the exception of Vögel's test, outlined above, which requires the use of ammonium sulphocyanide, amyl alcohol and ether), while that for the detection of nickel is considerably more delicate than anything hitherto proposed for this purpose.

For use in ordinary qualitative analysis in college laboratories where nickel-free cobalt salts are not supplied to students, the test may be modified in one of two ways in order to slightly decrease its delicacy. (1) The students may be told that unless the change of color is retarded over a minute nickel may be regarded as absent, or (2) by using, instead of a 5N sodium hydroxide solution, a 10N or 15N solution, when the delicacy is so decreased as to give practically no reaction for nickel in ordinary cobalt salt solutions.

I desire to express my sincere thanks to Dr. J. F. Snell for the valuable advice he has rendered during the progress of this work.

SYNTHESES OF DERIVATIVES OF QUINOLINE.

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Received March 28, 1904.

THE best method for the synthetical preparation of quinoline and its derivatives is that of Skraup,¹ which consists in heating an aromatic amine with glycerin, an aromatic nitro compound (usually nitrobenzene), and sulphuric acid. A quinoline ring is formed by the combining of the aromatic amine and the glycerin with loss of water and hydrogen. The nitro compound serves as an oxidizing agent, and is itself reduced to an amine from which quinolines are also formed, sometimes making mixtures that are difficult to separate.

¹ *Wien. Acad. Ber.*, **2**, 593 (1881); **2**, 1039 (1883).

The Skraup synthesis was extended by Doebner and Miller,¹ who substituted glycol for glycerin, and prepared quinaldine from aniline, glycol, nitrobenzene and sulphuric acid, and also prepared quinaldine and some of its derivatives from paraldehyde, aromatic amines, nitrobenzene, and sulphuric acid. Skraup also obtained quinaldine from crotonaldehyde, aniline, nitrobenzene, and sulphuric acid.² Later it was learned that an oxidizing agent was not necessary, when aldehyde was used, but that the synthesis could be carried out by heating the aromatic amine with aldehyde and concentrated hydrochloric acid on the water-bath.³

Still later Knueppel⁴ suggested a modification of the Skraup synthesis. In order to lessen the formation of tarry products, and to hinder the formation of more than one derivative of quinoline, he sought an inorganic oxidizing agent. Using arsenic oxide, he obtained very satisfactory results in syntheses in which he used an aromatic amine, glycerin, and sulphuric acid.

With these modifications in mind we have carried on experiments along three lines. First, we have used arsenic oxide as suggested by Knueppel to prepare some derivatives of quinoline that had not been prepared by this means, showing a wider application of his modification of the Skraup synthesis; second, we have prepared some derivatives of quinoline not previously described, by combining aromatic amines with aldehyde by heating with concentrated hydrochloric acid; third, we have used arsenic oxide as the oxidizing agent in preparing one derivative of quinaldine from an aromatic amine and glycol.

I. SUBSTANCES MADE FROM GLYCERIN AND AROMATIC AMINES,
USING As_2O_5 AS OXIDIZING AGENT.

p-Toluquinoline (*6*-Methylquinoline), $\text{C}_9\text{H}_6\text{N}.\text{CH}_3$.—Fifty grams *p*-toluidine, 140 grams glycerin, 130 grams concentrated sulphuric acid, and 66.5 grams arsenic oxide (As_2O_5) were heated for four hours on a sand-bath. The first reaction is quite violent and the flask must be removed from the bath until the violent reaction has ceased. The mixture is diluted with water, made alkaline with sodium hydroxide and distilled with steam. To dissolve any oil that has separated out, sulphuric acid is added; then

¹ *Ber. d. chem. Ges.*, **14**, 2812.

² *Ibid.*, **15**, 897.

³ *Ibid.*, **16**, 2465.

⁴ *Ibid.*, **29**, 704.

sodium nitrate in excess is put in to diazotize any unchanged primary amine. The solution is again made alkaline with sodium hydroxide, and distilled with steam. The *p*-toluquinoline is extracted with ether, and rectified, boiling-point 258°C ., agreeing with that given by Skraup,¹ 257.4° - 258.6°C . A determination of nitrogen gave 10.08 per cent.; calculated, 9.81.

o-Nitro-*p*-toluquinoline (*8*-nitro-6-methylquinoline), $\text{C}_9\text{H}_7\text{N}\cdot\text{CH}_3\cdot\text{NO}_2$.—Fifty grams *m*-nitro-*p*-toluidine, 100 grams glycerin, 50 grams sulphuric acid, and 50 grams arsenic oxide were warmed on a sand-bath till a vigorous reaction began. The flask was removed for a few moments till the violent reaction ceased, and was heated to gentle boiling for three hours. The mixture was then diluted with water and allowed to stand over night. The precipitate was removed and the filtrate made alkaline with sodium hydroxide. The base thus precipitated was dissolved in hydrochloric acid, warmed for several hours with animal charcoal and filtered. Ammonia gas was led into the hot filtrate, the precipitate formed was dissolved in hot alcohol, water added till a slight cloudiness appeared, when it was allowed to stand to crystallize. Light yellow needle-shaped crystals were obtained; melting-point 122° , agreeing with that assigned by Nölting and Troutman,² who prepared this substance, using picric acid as the oxidizing medium. A determination of nitrogen gave 15.40 per cent.; calculated, 14.89.

II. SUBSTANCES PREPARED FROM ALDEHYDE.

o-Nitro-*p*-methylquinaldine (*8*-nitro-2,6-dimethylquinoline), $\text{C}_9\text{H}_7\text{N}(\text{CH}_3)_2\text{NO}_2$.—Eighteen grams *m*-nitro-*p*-toluidine, 32 grams aldehyde, and 7 grams concentrated hydrochloric acid were heated on a water-bath for three hours. The product was diluted with water, made alkaline with sodium hydroxide, and steam passed through the solution till the distillate was no longer red in color. The solid residue in the flask was extracted with alcohol. The alcoholic solution was boiled with animal charcoal, filtered, and water added to precipitate the base. After recrystallizing from alcohol, orange-colored needles were obtained, melting-point 114° . These were insoluble in water and soluble in hot alcohol. A determination of the nitrogen gave 14.3 per cent.; calculated, 13.8.

¹ *Jahresbericht*, 1881, p. 911.

² *Ber. d. chem. Ges.*, **23**, 3669.

The Hydrochloric Acid Salt was prepared by precipitation from ether solution with dry hydrochloric acid gas. The resulting substance was a gray powder. A determination of the chlorine in this salt, by the method of Carius, gave 14.76 per cent.; calculated, 14.84.

CHLORINE AND BROMINE DERIVATIVES OF QUINALDINE.

p-Chlorquinaldine (6-chlor-2-methylquinoline), $C_9H_7N.CH_3.Cl$.—Fifteen grams *p*-chloraniline, 24 grams aldehyde, and 10 grams concentrated hydrochloric acid were heated on the water-bath for four hours. The contents of the flask were diluted with water and treated with sodium nitrite to remove any primary amine which might remain. Then, after heating on the water-bath till the odor of oxides of nitrogen had disappeared, the solution was made alkaline with sodium hydroxide and distilled with steam. The distillate was extracted with ether, and on evaporating the ether, there remained an oil, which crystallized in white flakes when rubbed with a glass rod. These turned yellow on exposure to the air, melting-point 91° . A determination of the chlorine gave 19.95 per cent.; calculated, 19.80.

The Hydrochloric Acid Salt was prepared by dissolving the compound in ether and precipitating with hydrochloric acid gas. It is a white powder without definite melting-point. A determination of chlorine gave 33.12 per cent.; calculated, 33.17.

m- (or *a*) Chlorquinaldine (5- (or 7) chlor-2-methylquinoline), $C_9H_7N.CH_3.Cl$.—When condensations are made with aldehyde and the meta derivatives of the aromatic amines, it is evident that two isomeric derivatives of quinaldine may be formed. A group in the meta position with respect to an amino group in the amine will, therefore, occupy position 5 or 7 of the quinoline formed. Fifteen grams *m*-chloraniline, 24 grams aldehyde, and 10 grams hydrochloric acid were heated on the water-bath for four hours. The contents of the flask were diluted with water, and treated as for 6-chlor-2-methylquinoline. Crystals were obtained which, after purification by redistillation with steam, melted at 78° . A determination of nitrogen gave 8.05 per cent.; calculated, 7.9.

o-Chlorquinaldine (8-chlor-2-methylquinoline), $C_9H_7N.CH_3.Cl$.—Fifteen grams *o*-chloraniline, 24 grams aldehyde, and 10 grams hydrochloric acid were treated as for 6-chlor-2-methylquinoline.

Crystals were obtained which melted at 64° , agreeing with the melting-point of the substance obtained from glycol, and described later in this article.

p-Bromquinaldine (6-brom-2-methylquinoline), $C_9H_7N.CH_3.Br$.—Twenty grams *p*-bromaniline, 23 grams aldehyde, and 10 grams hydrochloric acid were treated as in the synthesis of the corresponding chlorine derivative. White crystals were obtained that were readily volatile with steam, crystallizing from the distillate. They darken on exposure to the light, melting-point 96° – 97° . Analysis gave: Br, 36.05; N, 6.64. Calculated: Br, 36.03; H, 6.30.

A considerable quantity of tarry products is formed in the synthesis of the halogen derivatives in the manner described above. In one case, the 5- (or 7) chlor-2-methylquinoline, the product was increased about 30 per cent. by washing and drying the tarry residue remaining in the flask after distillation with steam, mixing it intimately with finely powdered zinc chloride and fusing the mixture in a porcelain dish. The melt was dissolved in dilute hydrochloric acid, then made alkaline with sodium hydroxide and distilled with steam as before.

III. QUINALDINE SYNTHESIS WITH GLYCOL AND ARSENIC ACID.

o-Chlorquinaldine (8-chlor-2-methylquinoline), $C_9H_7N.CH_3.Cl$.—We have been able to find but one instance in which glycol has been used in the Skraup synthesis¹ and it seemed worth while to try another, and to see whether glycol would form derivatives of quinaldine, and also whether arsenic oxide would serve as an oxidizing agent with glycol as well as with glycerin. Ten grams *o*-chloraniline, 9 grams glycol, 25 grams arsenic oxide and 25 grams concentrated sulphuric acid were heated to gentle boiling for four hours on a sand-bath. The contents of the flask were then diluted with water, diazotized, made alkaline with sodium hydroxide, and distilled with steam. Crystals were obtained, which were white at first, but turned yellow on exposure to the air, melting-point 64° . A determination of chlorine gave 19.8 per cent.; calculated, 19.95.

SUMMARY.

(1) Following Knueppel's modification of the Skraup synthesis, we have prepared 6-methylquinoline, and 8-nitro-6-methylquinoline, using arsenic oxide as the oxidizing medium.

¹ *Ber. d. chem. Ges.*, 14, 2814.

(2) We have prepared the following new substances from aldehyde and substituted amines: 8-Nitro-2,6-dimethylquinoline; 6-chlor-2-methylquinoline; 5- (or 7) chlor-2-methylquinoline; 8-chlor-2-methylquinoline; 6-brom-2-methylquinoline.

(3) We have prepared one derivative of quinaldine, 8-chlor-2-methylquinoline, from an aromatic amine and glycol, using arsenic oxide as the oxidizing medium.

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REVIEW.

Lubricating Greases.¹

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A SATISFACTORY examination or analysis of lubricating greases is, to say the least, tedious and complicated, even in a laboratory suitably equipped for this class of work, and I can readily appreciate the feeling of practical chemists, whose main chemical work around this section of the country is anything but greasy, when your manager sends you a tub of "grease," asking you to analyze the same, and tell him what it is made of, and if it is good for anything, and perhaps how it is made.

Before entering upon the chemical analysis and discussion of suitable methods, it might be well, as a practical introduction, to say a few words about greases in general, so as to acquaint you with the multitudinous materials or substances that enter, and are more or less used in compounding the numerous kinds and classes of lubricating greases found in the market.

The market price for these greases varies all the way from 1½ cents up to 15 cents per pound, and naturally the grease manufacturer uses, and has to use, very cheap or inferior materials to enable him to manufacture and sell at a profit, at such low figures, as the prices of the cheapest grades indicate; hence, the materials used for such cheap compounds are, to a large extent, waste materials or residues from petroleum distillation, mixed with waste fatty substances, and cheap inert mineral matter of all kinds and descriptions. On the other hand, the more expensive greases are generally compounded from good, pure materials suitable for the purpose. However, it should be borne in mind that a cheap grease, that is, the price of the grease, may not be any indication whatsoever as to the suitability of the grease for certain work any more than it follows that a more expensive grease would be any more suitable for certain kinds of work.

¹ Read before the Pittsburg Section of the American Chemical Society.