The mixture in the receiver was distilled at atmospheric pressure in an atmosphere of carbon dioxide. Two layers formed in the distillate—a lower cacodyl chloride layer and an upper aqueous layer. The lower cacodyl chloride layer was separated, washed with 100 ml. of water and dried over 20 g. of calcium chloride. There was obtained 150 g. of product (28% of theoretical based on potassium acetate), which had a boiling point of 106–109° at atmospheric pressure.

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RECEIVED JANUARY 8, 1947

The Skraup Reaction with Acrolein and its Derivatives. I. The Preparation of 6-Methoxy-8-nitroquinoline

BY HARRY L. YALE

The role of acrolein as an intermediate in the Skraup reaction has been accepted generally. The poor yield of quinoline from the product of the reaction between aniline and acrolein has been considered, however, as indirect evidence for another mechanism.[1] The Doebner–Miller modification of the Skraup reaction, which employs β-substituted acrolein derivatives, has been used with success in the preparation of 2-substituted quinolines and this has given additional weight to the probability that acrolein does exist, at least momentarily, during the Skraup reaction. Recently, Manske[2] has employed α-methylacrolein and its dimethyl acetal and Utermohlen[3] has used α-methylacrolein, α-ethylacrolein, their diacetates and dipropionates, to prepare a number of 3-substituted quinoline compounds. Quinoline compounds with alkyl substituents in the 4-position have been prepared by the reaction of alkyl vinyl ketones with aniline. In 1907, Blaise and Maire[4] reported that the condensation product of ethyl vinyl ketone and aniline gave 4-ethylquinoline on heating with aniline hydrochloride. Later, Prill and Walter[5] found that 4-substituted quinolines could be prepared in good yield by the reaction between methyl vinyl ketone, its homologs and derivatives, and an aromatic amine in the presence of sulfuric acid and an oxidizing agent such as nitrobenzene or arsenic acid. Recently Campbell and his associates[6] have further developed this modification of the Skraup reaction to prepare a number of lepidines.

Our interest in preparing 6-methoxy-8-nitroquinoline caused us to investigate the same reaction, employing acrolein in place of methyl vinyl ketone under somewhat milder conditions. We wish to report at this time that the desired quinoline derivative was obtained in 42.3% yield. Since aniline and acrolein under these conditions gave no more than traces of quinoline, it appears likely that some activation of the *ortho* hydrogen is necessary for ring closure.

Work is now in progress in these laboratories on the further development of this reaction.

Experimental

All melting points are uncorrected.

Preparation of 6-Methoxy-8-nitroquinoline.—An intimate mixture of 168 g. (1.0 mole) of 3-nitro-4-aminoanisole, 132 g. of arsenic pentoxide, 152 ml. of concentrated sulfuric acid and 72 ml. of water was heated to 80°. To this was added dropwise 70 ml. of acrolein during two hours, maintaining the temperature at 75–80°. After the addition of the acrolein, the mixture was heated to 120° during one hour, cooled, diluted to five liters with water and filtered. The filtrate was neutralized with ammonia and the precipitated 6-methoxy-8-nitroquinoline was collected on a filter and air dried. After purification it melted at 157° and a mixed melting point with an authentic sample of 6-methoxy-8-nitroquinoline, prepared by the Skraup reaction, was 157°. The yield was 86.5 g. or 42.3% of the theoretical amount.

Reaction between Aniline and Acrolein.—The reaction was carried out as above except that 93 g. (1.0 mole) of aniline was substituted for the 3-nitro-4-aminoanisole. Subsequent to heating the reaction mixture to 120°, it was diluted with water and made alkaline with 40% sodium hydroxide solution. A large amount of semi-solid black material separated. The mixture was steam distilled to isolate any quinoline as well as the unreacted aniline. The steam distillate was extracted with ether, the ether extracts were dried and the ether removed by distillation. The entire residual oil distilled at 79–82° (20 mm.), weighed 12.0 g. and was identified as aniline by conversion to the *p*-toluenesulfonanilide, m. p. 109–110°. The reported melting point of this compound is 112°.

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RECEIVED DECEMBER 18, 1946

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[1] Bergstrom, *Chem. Rev.*, **35**, 77 (1944); Manske, *ibid.*, **30**, 113 (1942).

[2] Manske, Marion and Leger, *Can. J. Research*, **B20**, 133 (1942).

[3] Utermohlen, *J. Org. Chem.*, **8**, 544 (1943).

[4] Blaise and Maire, *Compt. rend.*, **144**, 93 (1907); *Bull. soc. chim.*, [4] **3**, 667 (1908).

[5] Prill and Walter, U. S. Patent 1,806,563 and 1,806,564; *C. A.*, **25**, 3668 (1931).

[6] Campbell, *et al.*, THIS JOURNAL, **67**, 86 (1945); **68**, 1837 (1946); abstracts of the American Chemical Society, Chicago meeting, Sept. 9–13, 1946.

NEW COMPOUNDS

Methylammonium Sulfamate

Ten grams of sulfamic acid was dissolved in water and neutralized with aqueous methylamine. The water was removed under reduced pressure on a steam-bath and the warm liquid residue (quantitative yield) was crystallized from methyl alcohol and dried *in vacuo* at 75°. The dense white needles melted at 91–93° and were found to be deliquescent.

Anal. Calcd. for $CH_8O_3SN_2$: N, 21.87. Found: N, 21.9.

Solubility in 100 g. of boiling solvent: methyl alcohol, over 124 g.; 2-B anhydrous ethyl alcohol, 2.3 g. From ethyl alcohol it separates in thin clear plates, m.p. 91–93°.

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RECEIVED JANUARY 29, 1947

Some Esters of 2-Furoic Acid

The new compounds listed in Table I were prepared through the acid chloride.

Procedure.—Furoyl chloride was prepared by heating one mole (112 g.) of the acid[1] at 110–120° with a 15% excess of thionyl chloride until the evolution of hydrogen chloride ceased. The excess thionyl chloride was removed at the water pump and the residue distilled *in vacuo* to yield 90% (118 g.) of furoyl chloride boiling at 90° (20 mm.).

The benzyl and cyclohexyl esters were prepared by fluxing 0.5 mole (65 g.) of the acid chloride with 0.5 mole of the alcohol until evolution of hydrogen chloride ceased. The ester was purified by distillation *in vacuo*. The *t*-butyl ester was prepared by the general method in Organic Syntheses.[2]

TABLE I

Esters	B. p., °C.	Mm.	Yield, %	$n^{30}D$	Formula	Sapon. equiv. Calcd.	Found
t-Butyl	90	24	20	1.4639	$C_9H_{12}O_3$	168	167
Benzyl	141–142	2	41	1.5505	$C_{12}H_{10}O_3$	202	203
Cyclohexyl[a]	122–124	2	49	1.4499	$C_{11}H_{14}O_3$	194	194

[a] M. p. 32–33°.

Consistent analytical results on the benzyl ester could be obtained only by the method of Maglio.[3] The other esters gave no trouble on saponification.

Incidental to the preparation of the acid chloride, it was observed that the reaction mixture hydrolyzed very rapidly if moisture was not excluded. This phenomenon is in contrast to the pure halide which is hydrolyzed only very slowly by boiling water. Hartman and Dickey[4] call attention to the varying yields reported in the literature, and state that this may be due to impurities in the furoic acid and/or reagents used. Our observation would indicate that these impurities catalyze the hydrolysis and that the previously reported low yields may have been due to failure to exclude moisture.

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[1] The commercial 2-furoic acid generously supplied by the Quaker Oats Co. was used without further purification.

[2] "Organic Syntheses," **24**, 19 (1944).

[3] Maglio, *Chem. Analyst*, **25**, 39 (1946).

[4] Hartman and Dickey, *Ind. Eng. Chem.*, **24**, 151 (1932).

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p-Ethoxyphenylglyoxal

Eighty-two grams (0.5 mole) of *p*-ethoxyacetophenone in a mixture of 300 ml. of dioxane and 11 ml. of water was oxidized with 56 g. (0.5 mole) of selenium dioxide according to the method of Riley and Gray.[1] After working up in the usual manner, the product was fractionated through a 20-cm. Vigreux column at 103–105° (4 mm.) to give 38 g. (40.5%) of a yellow oil. The monosemicarbazone was prepared according to the directions of Shriner and Fuson.[2] The derivative could be crystallized from aqueous ethanol, m. p. 206–207° (dec.).[3]

Anal. (by Arlington Laboratories, Fairfax, Virginia). Calcd. for $C_{11}H_{13}N_3O_3$: C, 56.16; H, 5.57. Found: C, 56.56; H, 5.78.

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[1] Riley and Gray, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 509.

[2] Shriner and Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1946, p. 142.

[3] Melting points were taken with a Fisher–Johns apparatus.

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2-(*p*-Ethoxyphenyl)-quinoxaline

Two and three-tenths grams (0.01 mole) of *p*-ethoxyphenylglyoxal[1] in 25 ml. of glacial acetic acid was mixed with 2.2 g. of *o*-phenylenediamine, and treated according to the method of Fuson, *et al.*[2] The product was recrystallized twice from aqueous ethanol to give crystals melting at 128°.

Anal. (by Arlington Laboratories, Fairfax, Virginia). Calcd. for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19. Found: C, 76.39; H, 5.56; N, 11.57.

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RECEIVED FEBRUARY 3, 1947

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[1] Kipnis, Soloway and Ornfelt, THIS JOURNAL, **69**, 1231 (1947).

[2] Fuson, Emerson and Gray, *ibid.*, **61**, 482 (1939).

COMMUNICATIONS TO THE EDITOR

THE CRYSTAL STRUCTURE OF LITHIUM BOROHYDRIDE $LiBH_4$

Sir:

As a consequence of the remarks of Dr. H. C. Brown to one of us concerning the interest in the structure of lithium borohydride[1] and its commercial availability, we undertook an X-ray diffraction investigation of its crystal structure and are now making the following preliminary report of the results obtained.

Expiermentally, the density was found to be 0.66 g./cc. indicating the presence of four molecules per unit cell. Data obtained from rotation and oscillation photographs using CuKα radiation show that the unit cell of lithium borohydride is orthorhombic with the dimensions $a_0 = 6.81$, $b_0 = 4.43$ and $c_0 = 7.17$ kX. The density calculated from these cell dimensions is 0.666 g./cc.

An examination of the extinctions indicates that the arrangement of lithium and borohydride ions satisfies the symmetry of the space group Pcmn. Intensity calculations show that the hydrogens can make an appreciable contribution to the intensities and that a tetrahedral borohydride ion appears to be compatible with the data.

The spatial arrangement is such that each lithium ion is associated with four borohydride ions. Two of the lithium ions are separated from the boron by 2.56 kX and the other two by 2.47 kX.

[1] For a description of the properties of $LiBH_4$, see Schlesinger and Brown, THIS JOURNAL, **62**, 3429 (1940). The material used was purchased from the Lithaloys Corporation, 444 Madison Ave., New York, N. Y.