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).

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.

(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

(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 LiBH4

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.

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The angles between the lithium and boron vary from 97 to 116°. A tetrahedral arrangement of the hydrogens about the boron leads to an arrangement in which each lithium is surrounded by four hydrogen atoms which are arranged about it in the form of a distorted tetrahedron, each of the hydrogens being from a different borohydride group. The over-all structure of lithium borohydride may be described as that of strings of borohydride tetrahedra stacked edge on edge in the b direction of the crystal.

Lithium borohydride does not appear to be isomorphous with lithium aluminum hydride, lithium perchlorate, lithium fluoborate, or with the sulfates of magnesium and beryllium.

More complete details will be presented shortly.

DEPARTMENT OF CHEMISTRY P. M. HARRIS
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RECEIVED APRIL 18, 1947

THE COMPETITIVE INHIBITION OF THE METABOLISM OF α-AMINO ACIDS BY THEIR HALOGENATED ANALOGS

Sir:

A wild type strain of *Neurospora crassa* 8815-3a, has been used for testing a number of halogenated phenylalanines and tyrosines in respect to their capacities as growth inhibitors. Relative activities of the individual compounds were determined from the quantities of substance required to reduce the growth rate of the mold in growth tubes[1] to one-half of the normal value. The tubes contained 10 ml. of minimal medium[2] solidified with one per cent. agar and a small amount of the natural amino acid corresponding to the derivative being tested. Some of the results obtained are given in Table I.

INHIBITION OF GROWTH OF *Neurospora crassa* BY SOME HALOGENATED α-AMINO ACIDS

Compound	Mg./ml. for 50% inhibition[a]	moles inhibitor / moles amino acid
3-Fluoro-DL-phenylalanine	0.04	1.2
3-Fluoro-DL-tyrosine	.23	10.5
3-Fluoro-L-tyrosine	.15	6.8
3-Fluoro-D-tyrosine	.41	18.5

[a] Tubes for testing phenylalanine derivatives contained 0.03 mg./ml. of DL-phenylalanine; for tyrosine derivatives 0.02 mg./ml. of L-tyrosine.

It also has been shown that the inhibitory quotients for 2-chloro-, 3-chloro-, 4-chloro-, 3-bromo-, 3-iodo-DL-phenylalanine and for 3,5-difluoro-DL-tyrosine are greater than 150 and that the inhibitory action observed for all compounds is competitive in nature. Further it has been noted that effective inhibitors exhibit a high degree of specificity.

In respect to the inhibitory action of 3-fluoro-D-tyrosine and 3-fluoro-L-tyrosine the L-isomer is the more active of the two but in the presence of the D-isomer the mold produces considerable quantities of a dark brown pigment, an effect which is not observed with either the L-isomer or the racemic mixture. It is evident that the above actions must be interpreted in terms of at least two different systems concerned with the metabolism of tyrosine.

The most effective of the inhibitors described have not been tested on pure cultures of organisms other than *Neurospora*. However, it has been demonstrated that 3-fluoro-DL-phenylalanine is far more effective than sulfathiazole for inhibition of growth of those micellaneous airborne yeasts, molds and bacteria that can be obtained on exposed plates containing a yeast extract–agar medium.

The outstanding effectiveness of the monofluoro-phenylalanines and tyrosines as competitive inhibitors for their parent amino acids, and as antimetabolites, may be interpretable on simple steric grounds associated with the small size of the fluorine atom. In this connection it may be significant to consider the *p*-aminobenzoic acid reversal of the inhibition of growth of *E. coli* by 3-fluoro-*p*-aminobenzoic acid,[3] the apparent replacement of *p*-aminobenzoic acid by 2-fluoro-*p*-aminobenzoic acid[3] and the inhibition of acetate metabolism by fluoroacetate.[4]

Studies are now in progress on the effectiveness of the various isomeric monofluoro-tyrosines and phenylalanines as growth inhibitors in *Neurospora* and other biological systems and in extending the principles disclosed in the case of the above two α-amino acids to other α-amino acids.

(1) F. J. Ryan, G. W. Beadle, and E. L. Tatum, *Am. J. Bot.*, **30**, 784 (1943).

(2) G. W. Beadle and E. L. Tatum, *ibid.*, **32**, 678 (1945).

(3) (a) F. C. Schmelkes and M. Rubin, THIS JOURNAL, **66**, 1631 (1944); (b) O. Wyss, M. Rubin and F. B. Strandskov, *Proc. Soc. Exptl. Biol. Med.*, **52**, 155 (1943).

(4) (a) E. S. Guzman-Barron, G. R. Bartlett and G. Kalnitsky, *Proc. Fed. Am. Soc. Expll. Biol.*, **5**, 121 (1946); (b) E. S. Guzman-Barron and G. Kalnitsky, *Biol. Bull.*, **91**, 238 (1946).

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RECEIVED APRIL 5, 1947

THE DECARBONYLATION OF ETHYL PYRUVATE[1]

Sir:

The decarbonylation of α-keto-esters has importance in synthetic chemistry,[2] and related reactions are widely postulated in biochemical mechanisms. We have investigated one aspect of the mechanism of the thermal decarbonylation of ethyl pyruvate with the aid of C^{14}. Pyruvic ester labelled in the α carbon atom was synthesized by the following sequence of reactions:

(1) This paper is based on work performed under Contract #W-7405-Eng-48 with the Atomic Energy Commission in connection with the Radiation Laboratory, and the Department of Chemistry, University of California, Berkeley, California.

(2) "Org. Synth.," Coll. Vol. II, p. 531.