Butyl acetate, although an excellent solvent for the thiocyanate, should be used with care. The color produced by a given concentration of molybdenum appears to depend to no slight extent upon the manner in which the solvent has been saturated with the reagents. Figures 8 and 9 illustrate the type of results obtained with butyl acetate. It will be noted that the solvent which had been shaken with all three reagents changed color rapidly. The color of pure butyl acetate solutions of molybdenum thiocyanate likewise intensified, although not so rapidly or to so marked a degree. Butyl acetate which had been previously saturated with stannous chloride and hydrochloric acid under the conditions of the experiment behaved in a similar manner, although the intensity of the color was less during the first 12 hours.

Summary

Within the limits of the observations it is recommended that in the determination of molybdenum the concentration of hydrochloric acid be held at 5.0 per cent, potassium thiocyanate at 0.6 per cent, and stannous chloride above 0.1 per cent. Under some conditions sulfuric acid exerts an appreciable influence upon the color formation. Extraction of the complex should be made 5 minutes after adding the reagents. The behavior of the thiocyanate in ether, cyclohexanol, and butyl acetate has been studied. Anomalous color effects obtained with butyl acetate indicated that in general it was not as satisfactory an extractor for molybdenum as ether or cyclohexanol.

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An Optical Crystallographic Study of Some Derivatives of Barbital and Luminal

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CHEMICAL tests are not entirely satisfactory for the identification of some barbituric acid derivatives. Of these derivatives, two of the most commonly used are barbital (veronal or 5,5-diethyl barbituric acid) and phenobarbital (luminal or 5-ethyl-5-phenyl barbituric acid) for which optical crystallographic data are here presented. These data can be useful in the identification of these two medicinal substances. None of the derivatives presented in this paper, however, have been reported in the literature with the exception of the *p*-nitrobenzyl compounds, which have been prepared by Lyons and Dox (*3*), Hargreaves and Nixon (*1*), and Jesperson and Larsen (*2*).

Preparation and Analysis

A number of benzyl and phenacyl derivatives were prepared from barbital and phenobarbital in the following manner:

Equivalent amounts of the barbituric acid and potassium or sodium carbonate were dissolved in a little more than enough boiling water to make a saturated solution. This solution was added to a solution of the benzyl or phenacyl halide (two molecular quantities) dissolved in an amount of alcohol twice as large as the amount of water used to dissolve the barbituric acid salt. The resulting mixture was refluxed until the reaction was completed.

The *o*-chlorobenzyl and the phenacyl derivatives of phenobarbital were prepared, but were obtained in the form of oily liquids which could not be made to crystallize. The *p*-chlorobenzyl derivative of phenobarbital occurs in two forms, depending on the method used for purification. If crystallization is caused to take place from a hot saturated solution, form A (Tables I and II) is obtained; but if the crystallization takes place slowly from a less saturated solution, we obtain form B.

Each new compound was analyzed for halogens or nitrogen. The melting points were run by both the tube method and the "Bloc Maquenne" method. Water of crystallization was not present in any of the compounds prepared.

Table I. Derivatives of Barbital and Phenobarbital

Derivative	Formula	Crystal Habit	Color	Halogen		Melting Point Uncorrected	
				Calcd.	Found[a]	Tube	Block
				%	%		
			Barbital				
o-Bromobenzyl	$C_{22}H_{22}N_2O_3Br_2$	Thick rods	White	30.62	30.50	140	141
m-Bromobenzyl	$C_{22}H_{22}N_2O_3Br_2$	Thin plates	White	30.62	30.57	91	90
p-Bromobenzyl	$C_{22}H_{22}N_2O_3Br_2$	Flat rods and plates	White	30.62	30.65	146	147
o-Chlorobenzyl	$C_{22}H_{22}N_2O_3Cl_2$	Long rods	White	16.37	16.49	127	125
m-Chlorobenzyl	$C_{22}H_{22}N_2O_3Cl_2$	Thin plates	White	16.37	16.34	102	100.5
p-Chlorobenzyl	$C_{22}H_{22}N_2O_3Cl_2$	Flat rods and plates	White	16.37	16.32	142	144
p-Iodobenzyl	$C_{22}H_{22}N_2O_3I_2$	Rods and thick plates	White	40.55	40.48	122	123
m-Nitrobenzyl	$C_{22}H_{22}N_4O_7$	Long needles	Pale yellow	12.34[b]	12.27[b]	159	160
p-Nitrobenzyl	$C_{22}H_{22}N_4O_7$	Needles and rods	Pale yellow	12.34[b]	12.29[b]	192	193
Phenacyl	$C_{24}H_{24}N_2O_5$	Flat rods and plates	White	6.67[b]	6.72[b]	191	192
p-Bromophenacyl	$C_{24}H_{22}N_2O_5Br_2$	Rods	White	27.65	27.55	191.5	193
			Phenobarbital				
o-Bromobenzyl	$C_{26}H_{22}N_2O_3Br_2$	Short rods	White	28.04	27.98	116	113
m-Bromobenzyl	$C_{26}H_{22}N_2O_3Br_2$	Thin plates	White	28.04	28.14	130	130
p-Bromobenzyl	$C_{26}H_{22}N_2O_3Br_2$	Thin plates, twinned	White	28.04	28.05	117	118
m-Chlorobenzyl	$C_{26}H_{22}N_2O_3Cl_2$	Thin plates	White	14.74	14.90	111	111
p-Chlorobenzyl	$C_{26}H_{22}N_2O_3Cl_2$ A	Thin plates, twinned	White	14.74	14.63	111	111
	B	Thick plates	White	14.74	14.64	113	114
p-Iodobenzyl	$C_{26}H_{22}N_2O_3I_2$	Thick plates and rods	White	37.77	37.90	127–8	127
m-Nitrobenzyl	$C_{26}H_{22}N_4O_7$	Flat rods and plates	Pale yellow	11.16[b]	11.17[b]	149.5	151
p-Nitrobenzyl	$C_{26}H_{22}N_4O_7$	Rods and needles	Yellow	11.16[b]	11.20[b]	182.5	184
p-Bromophenacyl	$C_{28}H_{22}N_2O_5Br_2$	Rods and needles	White	25.53	25.65	164	167

[a] Average of two determinations.
[b] Per cent nitrogen.

TABLE II. OPTICAL CRYSTALLOGRAPHIC DATA FOR DERIVATIVES OF BARBITAL AND PHENOBARBITAL

(All monoclinic)

Derivative	Optical Characteristic (Sign)	Sign of Elongation	Refractive Indices at 25°: Alpha	Beta	Gamma	Rhombic Dispersions	Extinction Angle, Degrees
			Barbital				
o-Bromobenzyl	−	+	1.556	1.640	1.663	None	16
m-Bromobenzyl	−	+	1.577	1.679	1.693	None	30
p-Bromobenzyl	+	−	1.556	1.577	1.698	None	4
o-Chlorobenzyl	−	+	1.548	1.649	1.696	None	20
m-Chlorobenzyl	−	+	1.538	1.640	1.690	None	23
p-Chlorobenzyl	+	−	1.545	1.563	1.664	None	33
p-Iodobenzyl	+	−	1.531	1.642	$>CH_2I_2$	None	34
m-Nitrobenzyl	−	−	1.487	1.626	1.715	Strong $\nu > \rho$	7
p-Nitrobenzyl	±	+	1.510	1.606	1.706	Strong	14
Phenacyl	−	+	1.587	1.626	1.634	Moderate $\rho > \nu$	42
p-Bromophenacyl	−	+	1.599	1.642	1.649	None	32
			Phenobarbital				
o-Bromobenzyl	+	±	1.605	1.620	1.720	Moderate $\nu > \rho$	36
m-Bromobenzyl	−	−	1.599	1.668	1.698	None	7
p-Bromobenzyl	[a]	+	1.563	[a]	$>CH_2I_2$	[a]	9
m-Chlorobenzyl	−	−	1.580	1.660	1.681	None	5
p-Chlorobenzyl A	[a]	+	[a]	1.568	$=CH_2I_2$	[a]	8
B	+	±	1.585	1.593	1.730	None	15
p-Iodobenzyl	−	±	1.580	1.730	$>CH_2I_2$	Moderate $\nu > \rho$	34
m-Nitrobenzyl	−	+	1.538	1.652	1.715	Moderate $\nu > \rho$	25
p-Nitrobenzyl	−	+	1.534	1.666	$=CH_2I_2$	Strong $\nu > \rho$	17
p-Bromophenacyl	+	−	1.599	1.656	1.703	Strong $\nu > \rho$	36

[a] Since no optic axis interference figure could be seen, these values could not be determined.

Eleven derivatives of barbital and nine derivatives of phenobarbital were prepared, purified, and analyzed. The results are presented in Table I.

OPTICAL CRYSTALLOGRAPHIC DATA. The optical properties of each compound listed in Table I were determined by methods used in a similar study for compounds of strychnine (*4*) and cinchonine (*5*), and are presented in Table II. The optical properties of the derivatives of barbital differ sufficiently from those of phenobarbital to allow the use of the optical data in the identification of the original barbituric acid.

Summary

Ten new derivatives of barbital and eight new derivatives of phenobarbital have been prepared and described. The optical crystallographic data for twenty benzyl and phenacyl compounds of barbital and phenobarbital have been determined.

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Surface Tension between Aqueous and Isopropyl Ether Solutions of Acetic Acid

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THE factors determining the rate of extraction of acetic acid from aqueous solution by isopropyl ether and the efficiencies of types of equipment applicable to the extraction operation are under investigation in this laboratory. These form one phase of an investigative program directed toward the development of methods and data for the rational design of liquid-liquid extraction systems. Results thus far obtained show that the rate of extraction and, consequently, the efficiency of liquid-liquid contact equipment in which one solvent phase is dispersed may be primarily influenced by the interfacial surface tension between the two solvents. It is apparent that this result is logically explained by the fact that for a given volume of liquid the degree of dispersion and droplet size (hence contact area) are determined primarily by interfacial surface tension. Since the concentration of the soluble component distributing itself between two immiscible solvents in contact may exert a very considerable influence on their interfacial surface tension, the extent or efficiency of extraction in a given equipment is a function of the respective solute concentrations in the two phases, operating conditions and concentration gradient being otherwise fixed. Thus, in the extraction of acetic acid from water solution by isopropyl ether, the capacity coefficients in a tower of the spray type and the plate efficiencies of a bubble plate column are dependent upon the respective acid concentration of the two phases. A similar result for other types of contacting devices is also to be expected.

To permit a correlation of the results on this system the surface tension of different concentrations of aqueous acetic acid against isopropyl ether of varying acetic acid concentra-