Anal. Calcd. for $C_{20}H_{22}O_5$: C, 70.14; H, 6.48; mol. wt. (Rast), 342.2. Found: C, 70.04, 69.85; H, 6.21, 6.42; mol. wt. (Rast), 336.3.

Mameli,[5] who was the first to describe this ether, found that it was formed when an ether solution of the alcohol was left for many weeks in contact with traces of inorganic salts, and gave its m. p. as 88°.

Summary

1. By the addition of hydrobromic acid to safrole, 1-piperonyl-1-bromoethane has been prepared and from this the corresponding alcohol.

2. The Grignard reaction applied to the bromide, in the presence of acetone, yielded a mixture of 1-piperonylethanol-1, 2-methyl-3-piperonylbutanol-2 and 2,3-dipiperonylbutane.

3. This butanol has been converted by the action of sulfuric acid into the corresponding butene and 1,1,2-trimethyl-5,6-methylenedioxyindane.

4. From isosafrole and hydrobromic acid, *alpha*-ethylpiperonyl bromide has been obtained. The corresponding alcohol, from piperonal and ethylmagnesium bromide, has been shown to lose water on standing, with formation of the ether.

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(5) Mameli, *Rend. Accad. Lincei*, [5] **13**, II, 612 (1904); *Gazz. chim. ital.*, **35**, II, 32 (1905).

[CONTRIBUTION FROM THE BURROUGHS WELLCOME AND CO., U. S. A., EXPERIMENTAL RESEARCH LABORATORIES]

Some N-Aryl Barbituric Acids. II

BY JOHANNES S. BUCK

The present work is a continuation of that described in an earlier paper.[1] Two further series of 1-aryl-5,5-dialkyl barbituric acids have been prepared, the aryl groups being, as before, phenyl, *o*-, *m*- and *p*-tolyl, *o*-, *m*- and *p*-anisyl, *o*-, *m*- and *p*-phenetyl, and α- and β-naphthyl, while the alkyl groups are now 5,5-ethyl-isobutyl and 5,5-ethyl-isoamyl. The alkyl groups were selected to allow comparison, pharmacologically, with a series of isoalkylaryl ureas at present under examination.

Since the sodium salts of the N-aryl barbituric acids show a tendency to hydrolyze in aqueous solution, a number of barbituric acids having a dialkylamino group on the phenyl ring was prepared. These compounds are soluble both in alkaline and in acid solution. The presence of the dialkylamino group should also facilitate the resolution of those barbituric acids which carry, in addition to this group, an asymmetric carbon atom.

The two phenyl compounds have been previously described by Hjort and Dox;[2] the others are new. The pharmacological data will be given later in another place.

Experimental

Ethyl isobutylethylmalonate[3] and ethyl isoamylethylmalonate[3] were prepared by the action of the isoalkyl iodide on ethyl ethylmalonate, in the presence of sodium ethylate. It was found advantageous to carry out the reaction as rapidly as possible and to shake the crude ester several times with 5% sodium hydroxide solution.[4] After fractionation under reduced pressure the isobutyl compound boiled at 128.5–130° (15 mm.) (yield 71%) and the isoamyl compound at 126–127° (7.5 mm.) (yield 64%).

The condensation of the ester with the aryl urea and the subsequent purification were carried out substantially as previously described.[1] The procedure was modified in the case of the dialkylamino compounds, the cold reaction mixture being diluted, extracted with ether when possible, and saturated with carbon dioxide to precipitate the product, which was purified by recrystallization from aqueous alcohol, and usually also from ethyl acetate–hexane. No particular trouble was encountered except with 1-*m*-phenetyl-5,5-ethyl-isoamyl barbituric acid which was very difficult to obtain crystalline.

The barbituric acids are tabulated below. They are all white, crystalline, tasteless compounds, soluble in cold 5% sodium hydroxide solution, practically insoluble in water, slightly soluble to insoluble in petroleum ether, soluble in ether, soluble in alcohol, moderately to readily soluble in benzene, and readily soluble in ethyl acetate. In addition, the dialkylamino compounds dissolve readily in 5% hydrochloric acid. The solvents used for purification are given in the order used. Three or more crystallizations were generally necessary. In the tables the appearance described is that of the bulk specimen, crystallized from the last solvent given. The appearance varies greatly with solvent, etc.

The ureas are the same as those previously used.[1] Dimethylaminophenyl urea and diethylaminophenyl urea were prepared by the action of potassium cyanate on the amine hydrochloride in aqueous solution.

(1) Buck, THIS JOURNAL, **58**, 1284 (1936).

(2) Hjort and Dox, *J. Pharmacol.*, **35**, 155 (1929).

(3) Shonle and Moment, THIS JOURNAL, **45**, 243 (1923).

(4) *Cf.* Michael, *J. prakt. Chem.*, [2] **72**, 537 (1905).

TABLE I

1-ARYL-5,5-ETHYL-ISOBUTYL BARBITURIC ACIDS

Legend: A = alcohol; aA = aqueous alcohol; B = benzene; E = ether; Ea = ethyl acetate; H = hexane; P = petroleum ether.

Aryl radical	Appearance	M.p., °C.	Solvents recryst.	Formula	Analyses, %N Calcd.	Found
Phenyl[2]	Nodules of tiny prisms	149	aA, BP	$C_{16}H_{20}O_3N_2$	9.72	9.80
o-Tolyl	Cryst. powder (small prisms)	134	A, aA	$C_{17}H_{22}O_3N_2$	9.27	9.47
m-Tolyl	Broken cryst. crusts	138.5	aA, BP	$C_{17}H_{22}O_3N_2$	9.27	9.33
p-Tolyl	Soft crusts of prisms	149.5	A	$C_{17}H_{22}O_3N_2$	9.27	9.36
o-Anisyl	Nodules of tiny felted needles	176–177	aA, BP	$C_{17}H_{22}O_4N_2$	8.80	8.80
m-Anisyl	Bulky powder (small nodules)	139.5	aA, EaH	$C_{17}H_{22}O_4N_2$	8.80	8.94
p-Anisyl	Broken cryst. crusts	149	aA, BP	$C_{17}H_{22}O_4N_2$	8.80	8.92
o-Phenetyl	Broken crusts (tiny prisms)	142–143	aA, BH, A	$C_{18}H_{24}O_4N_2$	8.43	8.46
m-Phenetyl	Chalky powder (tiny nodules)	125.5	A, EaH	$C_{18}H_{24}O_4N_2$	8.43	8.42
p-Phenetyl	Chalky powder (clumps of needles)	145	A, BP	$C_{18}H_{24}O_4N_2$	8.43	8.38
α-Naphthyl	Finely cryst. powder	158	aA, BH, EaH	$C_{20}H_{22}O_3N_2$	8.28	8.31
β-Naphthyl	Bulky chalky powder	161–162	aA, BH	$C_{20}H_{22}O_3N_2$	8.28	8.46

TABLE II

1-ARYL-5,5-ETHYL-ISOAMYL BARBITURIC ACIDS

Aryl radical	Appearance	M.p., °C.	Solvents recryst.	Formula	Analyses, %N Calcd.	Found
Phenyl[2]	Thick friable crusts	129	aA, BH	$C_{17}H_{22}O_3N_2$	9.27	9.33
o-Tolyl	Finely cryst. powder	119	aA, EaH	$C_{18}H_{24}O_3N_2$	8.86	8.80
m-Tolyl	Finely cryst. powder	113–114	aA, EaH	$C_{18}H_{24}O_3N_2$	8.86	9.05
p-Tolyl	Chalky nodules	115	aA, BH	$C_{18}H_{24}O_3N_2$	8.86	9.06
o-Anisyl	Felted small needles	134	aA, BH, EaH	$C_{18}H_{24}O_4N_2$	8.43	8.35
m-Anisyl	Starchy cryst. powder	115–116	aA, EaH	$C_{18}H_{24}O_4N_2$	8.43	8.55
p-Anisyl	Chalky tiny nodules	120	aA, BP	$C_{18}H_{24}O_4N_2$	8.43	8.56
o-Phenetyl	Bulky nodules (tiny prisms)	162–163	aA, BP	$C_{19}H_{26}O_4N_2$	8.09	8.13
m-Phenetyl	Soft clumps of tiny nodules	72–74	EaH, EP	$C_{19}H_{26}O_4N_2$	8.09	8.40
p-Phenetyl	Coarse powder (prism nodules)	100–101	aA, BP	$C_{19}H_{26}O_4N_2$	8.09	8.25
α-Naphthyl	Bulky small nodules	193–194	BP, aA	$C_{21}H_{24}O_3N_2$	7.95	8.01
β-Naphthyl	Small nodules (clumps of prisms)	138	aA, EaH	$C_{21}H_{24}O_3N_2$	7.95	8.06

TABLE III

1-DIALKYLAMINOPHENYL-5,5-DIALKYL BARBITURIC ACIDS

Aryl radical	Alkyl radical	Appearance	M.p., °C.	Formula	Analyses, %N Calcd.	Found
p-Dimethylaminophenyl	Diethyl	Small pearly leaves	182	$C_{16}H_{21}O_3N_3$	13.85	13.80
p-Dimethylaminophenyl	Ethyl-*n*-butyl	Glitt. small flat prisms	157	$C_{18}H_{25}O_3N_3$	12.68	12.92
p-Dimethylaminophenyl	Ethyl-isobutyl	Bulky clumps of flat prisms	153	$C_{18}H_{25}O_3N_3$	12.68	12.83
p-Dimethylaminophenyl	Ethyl-isoamyl	Aggregates of small nodules	130	$C_{19}H_{27}O_3N_3$	12.16	12.17
p-Diethylaminophenyl	Diethyl	Small silky needles	175	$C_{18}H_{25}O_3N_3$	12.68	12.85
p-Diethylaminophenyl	Ethyl-*n*-butyl	Bulky fluffy powder	125.5	$C_{20}H_{29}O_3N_3$	11.69	11.83
p-Diethylaminophenyl	Ethyl-isobutyl	Broken crusts of small needles	140–141	$C_{20}H_{29}O_3N_3$	11.69	11.61
p-Diethylaminophenyl	Ethyl-isoamyl	Broken crusts (nodules)	125	$C_{21}H_{31}O_3N_3$	11.25	11.47

Dimethylaminophenyl Urea.—Slender striated needles (pale violet tint) from hot water; slightly soluble ether and benzene, soluble alcohol, insoluble petroleum ether, soluble cold 5% hydrochloric acid; no taste; m. p. 183°. *Anal.* Calcd. for $C_9H_{13}ON_3$: N, 23.45. Found: N, 23.60.

Diethylaminophenyl Urea.—Felted, slender, glittering needles (gray-violet tint) from hot water; soluble hot benzene, soluble alcohol, insoluble petroleum ether, soluble cold 5% hydrochloric acid; no taste; m. p. 136.5°. *Anal.* Calcd. for $C_{11}H_{17}ON_3$: N, 20.27. Found: N, 20.52.

The analyses (micro-Dumas) were carried out by Mr. W. S. Ide. The melting points are corrected.

Summary

1. To complete previous work, a series of 1-aryl-5,5-ethyl-isobutyl barbituric acids and a series of 1-aryl-5,5-ethyl-isoamyl barbituric acids have been prepared, the N-aryl groups in both series being phenyl, *o*-, *m*- and *p*-tolyl, *o*-, *m*- and *p*-anisyl, *o*-, *m*- and *p*-phenetyl and α- and β-naphthyl.

2. A series of acid-soluble barbituric acids was prepared in which the N-aryl groups were *p*-dimethylaminophenyl and *p*-diethylaminophenyl. The 5,5-dialkyl groups were diethyl, ethyl-*n*-butyl, ethyl-isobutyl and ethyl-isoamyl.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF BUFFALO]

Oxalato Complex Compounds of Tervalent Manganese

BY G. H. CARTLEDGE AND W. P. ERICKS

Complex compounds containing manganese in the tervalent or quadrivalent state have been prepared in a few instances, but there has never been a thoroughgoing study of the field, such as has been made in the compounds of chromium and cobalt. From a consideration of the structure of the manganese atom there is every reason to expect it to form complexes readily, since the manganic ion has the combination of available *d*, *s* and *p* eigenfunctions which is required for the formation of covalent bonds, according to the theory of Pauling.[1] That so few of such possible compounds have been prepared is readily ascribed to the complicated oxidation–reduction relations of manganese. The simple manganic ion is like the cobaltic ion in its large oxidation potential, but is even more difficult to manipulate because of the readiness with which it dismutates into the manganous ion and manganese dioxide.

The oxalato complexes are of particular interest in connection with the kinetics of the reaction between potassium permanganate and oxalates.[2] Potassium trioxalatomanganiate, $K_3[Mn(C_2O_4)_3]\cdot 3H_2O$, seems to have been prepared first by Souchay and Lenson.[3] Kehrmann[4] rediscovered the compound and isolated it in crystalline form. Meyer and Schramm[5] in 1922 attempted to prepare dioxalatodiaquomanganiates, but without success. Instead, they were able to obtain the corresponding dimalonatodiaquamanganiate, which is a fairly stable compound and readily prepared. In 1926 the same authors[6] reported that by treating cold sodium tetroxalate (in excess) with manganese dioxide they obtained an impure green material. This product was very unstable, turned yellowish-brown, and decomposed before it could be isolated for analysis. Meyer and Schramm concluded from analogy with the green sodium dimalonatodiaquomanganiate that the unstable product was the corresponding oxalato complex.

We have been able to prepare a number of pure compounds containing the trioxalatomanganiate and dioxalatodiaquomanganiate ions, as well as a difluodioxalato compound and, unexpectedly, a dioxalatodihydroxo complex of quadrivalent manganese. The oxalatomanganiates have turned out to be extremely interesting in that in aqueous solution they are easily converted one into the other, according to the reversible reaction

$$[Mn(C_2O_4)_3]^{=} + 2H_2O \rightleftharpoons [Mn(C_2O_4)_2(H_2O)_2]^{-} + C_2O_4^{-}$$

Using a spectrophotometric procedure we have been able to measure the equilibrium constant for this reaction, as will be shown in the following paper. The complexes are far more reactive than the corresponding chromium or cobalt compounds, but when properly isolated in pure form may be analyzed accurately and, in some instances, may be preserved indefinitely in a refrigerator.

Potassium Trioxalatomanganiate.—Our interest in the oxalato complexes arose from a need for some potassium trioxalatomanganiate of extreme purity, with particular reference to its freedom from iron. Trioxalato complexes are formed by tervalent chromium, iron and cobalt; the salts are all probably isomorphous with the manganic complex, and all of them have moderately high solubilities. Because of the instability of the manganic complex the principal purification is necessarily applied to the reagents rather than to the final product. We have accordingly devised a procedure which involves as few reagents as possible. The chief difficulty in obtaining a homogeneous product is due to the sparing solu-

(1) Pauling, THIS JOURNAL, **53**, 1367 (1931).

(2) Schilow, *Ber.*, **36**, 2735 (1903); Skrabal, *Z. anorg. Chem.*, **42**, 73 (1904); Schröder, *Z. öffentl. Chem.*, **16**, 270 (1910); Kolthoff, *Z. anal. Chem.*, **64**, 185 (1924); Deiss, *Z. angew. Chem.*, **39**, 664 (1926); Launer, THIS JOURNAL, **55**, 865 (1933); Launer and Yost, *ibid.*, **56**, 2571 (1934); Fessenden and Redmon, *ibid.*, **57**, 2246 (1935).

(3) Souchay and Lenson, *Ann.*, **105**, 254 (1858).

(4) Kehrmann, *Ber.*, **20**, 1594 (1887).

(5) Meyer and Schramm, *Z. anorg. Chem.*, **123**, 56 (1922).

(6) Meyer and Schramm, *ibid.*, **157**, 196 (1926).