Experimental

4,5-Dibromoguaiacol can be purified by boiling with 20% NaCl solution. The melting point of the substance prepared by this steam distillation is 94–95°. Methylation yields 4,5-dibromoveratrol, m.p. 92–93°. Dibromoguaiacol acetate melts at 101–102° in accordance with the value of Raiford and Silker[2]; m.p. of the benzoate 112–113° (Raiford and Silker[2] 110–111°).

Reduction of Tribromoguaiacol (II) with Zinc Dust and Acetic Acid.—Fourteen grams of tribromoguaiacol, 9 g. of zinc dust, 40 ml. of glacial acetic acid and 10 ml. of water were boiled under reflux for 4 minutes. The mixture was cooled, filtered and pieces of ice added. The oily precipitation solidified. The substance was filtered by suction, dried in vacuum (6 g.), triturated with petrol ether (b.p. 60–110°), filtered by suction and recrystallized from petrol ether; m.p. 94–95°.

Anal. Calcd. for $C_7H_6O_2Br_2$: Br, 56.73. Found: Br, 57.06, 56.87.

The melting points of its acetate, benzoate and methyl ether were in agreement with the values given above.

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Some 5-Alkyl-1-acetyl-2-thiohydantoins[1]

BY J. F. R. KUCK, J. J. HERDA, W. E. KOVAC AND J. V. KARABINOS

In the course of some work on the chromatography of amino acid derivatives in this Laboratory, we found it necessary to prepare 5-alkyl-1-acetyl-2-thiohydantoins from a number of α-amino acids. Although several of these derivatives were known, we wish to report the preparation of additional ones and describe a method for obtaining crystalline derivatives of most of the naturally occurring monoamino-monocarboxylic acids, essentially according to the directions of Johnson and Nicolet.[2]

TABLE I

5-ALKYL-1-ACETYL-2-THIOHYDANTOINS R—CH—CO—NH—CS—N—COCH$_3$

R-	Amino acid	M.p., °C.	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Isopropyl-	DL-Valine	115	47.98	47.92	6.04	6.27
n-Butyl-	DL-Norleucine	136	50.44	50.63	6.58	6.89
s-Butyl-	DL-Isoleucine	163	50.44	50.62	6.58	6.61
Methylthioethyl-	DL-Methionine	104	41.35	41.50	5.21	5.22
β-Amidoethyl-	L-Glutamine[a]	219	41.91	42.24	4.84	4.90
Indole-β-methyl-	DL-Tryptophan	170	58.52	58.50	4.56	4.27
p-Hydroxybenzyl-	L-Tyrosine[a]	248[b]	54.53	54.73	4.58	4.26
Hydrogen	Glycine	179[c]	37.96	38.21	3.82	3.63
Bis-thiomethyl-	L-Cystine[a]	208[d]				
s-Acetylthiomethyl-	L-Cysteine[a]	142[e]				
i-Butyl-	DL-Leucine[a]	129[f]				
Benzyl-	DL-Phenylalanine[a]	170[g]				
Amidomethyl-	DL-Asparagine[a]	224[g]				
Methyl-	DL-Alanine[a]	166[g]				

[a] Actually the optical identity of these acetylthiohydantoins is uncertain since acetic anhydride frequently acts as a racemizing agent. Furthermore the optical configuration of some of the amino acids was not given in the original reference and can only be surmised. [b] The oil which was precipitated by adding water was dissolved in 10 ml. of 5% sodium hydroxide and the yellow solution was filtered. The chilled filtrate was added slowly with stirring to a slight excess of 10% hydrochloric acid. The amorphous solid which separated was recrystallized from ethanol. The preparation reported was obtained only once; this procedure usually gave the unacetylated compound, 5-*p*-hydroxybenzyl-2-thiohydantoin of m.p. 211°. *Cf.* M. Jackman, *et al.*, THIS JOURNAL, **70**, 2884 (1948). [c] T. B. Johnson and B. H. Nicolet, *ibid.*, **33**, 1973 (1911). [d] B. H. Nicolet, *J. Biol. Chem.*, **88**, 395 (1930). [e] *Ibid.* [f] P. Schlack and W. Kumpf, *Z. physiol. Chem.*, **154**, 125 (1926). [g] Ref. 2.

One-hundredth of a mole of amino acid was heated with 0.9 g. of ammonium thiocyanate in 10 ml. of acetic anhydride containing 1.3 ml. of acetic acid for 30 minutes at 100°. After the reaction mixture was poured into 50 ml. of water an oil separated from which the acetylthiohydantoin subsequently crystallized. Further purification was accomplished by recrystallization of the crude product from ethanol. For purposes of identification the melting points and analyses of the derivatives prepared in this study are listed in Table I along with the others previously reported. The amino acids which failed to give a precipitate upon addition to water included DL-serine, DL-threonine, L-tyrosine, L-proline and L-hydroxyproline as well as the monohydrochlorides of L-histidine, L-arginine, DL-lysine and DL-ornithine. This may indicate the use of this reaction for the group separation of mixtures of the amino acids.

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The Action of Sodium on Di-*s*-butylmercury

BY JOHN F. LANE AND STEPHEN E. ULRICH

Previous studies in these laboratories[1,2] have shown that the major path of reaction in syntheses of the Wurtz type with *s*-alkyl halides proceeds through (ionic) interaction of an *s*-alkyl sodium with the halide. These studies have not, however, ruled out the possibility that a portion, at least, of the Wurtz product might have resulted from the dimerization of *s*-alkyl radicals formed by thermal dissociation of the *s*-alkyl sodium present, an energetically plausible process.[3] To throw further light upon this matter a study was undertaken on the interaction of sodium with di-*s*-butylmercury, in the hope of producing *s*-butylsodium through displacement of mercury. The interaction of sodium with mercury *n*-alkyls is

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[1] Research supported by the Office of Naval Research under contract N7ONR-449.

[2] T. B. Johnson and B. H. Nicolet, *Am. Chem. J.*, **49**, 197 (1913).

[1] S. E. Ulrich, F. H. Gentes, J. F. Lane and E. S. Wallis, THIS JOURNAL, **72**, 5127 (1950).

[2] J. F. Lane and S. E. Ulrich, *ibid.*, **72**, 5132 (1950).

[3] *Cf.* N. G. Brink, J. F. Lane and E. S. Wallis, *ibid.*, **65**, 943 (1943).

well-known[1,3] to produce *n*-alkyl sodium compounds in good yield

$$R_2Hg + 2Na \longrightarrow 2NaR + Hg$$

When an excess of sodium was allowed to react with di-*s*-butylmercury at 20–25° in *n*-dodecane, a reaction occurred in which after four hours, 95% of the theoretical quantity of mercury was set free. Carbonation of the reaction mixture gave, however, only a small amount (<5%) of the expected methylethylacetic acid, together with a small amount of methylethylmalonic acid. Direct interaction of sodium with di-*s*-butylmercury in the absence of a solvent led to a slow reaction which produced butane and butene, but no detectable trace of 3,4-dimethylhexane. Again the displacement of mercury by sodium was virtually quantitative.

These results indicate that *s*-alkyl sodium compounds are relatively unstable, a result in accord with previous observations of Morton and coworkers[4] that carbonation of the mixtures obtained when 2-chloro-3-methylbutane, 2-chlorobutane and 2-chloropentane were treated with sodium led to the production of only small quantities of the expected acids. The results further demonstrate that the thermal decomposition of such substances (*s*-R–Na) does not lead to any detectable quantity of dimeric (Wurtz) product $(s\text{-R-})_2$, but rather to products of disproportionation (R–H, olefin). Accordingly, it does not seem likely that any significant quantity of the dimeric product of the Wurtz reaction of an *s*-alkyl halide can arise from thermal dissociation of the intermediate *s*-alkyl sodium.

Experimental

Di-*s*-butylmercury.—This compound, b.p. 51–54° (2 mm.), was prepared in 64% yield by the procedure of Marvel and Calvery[5] with improvements by Gilman and Brown.[6] Analysis according to Whitmore and Sobatzki[7] indicated a purity of 97%.

Carbonation of *s*-Butylsodium.—To 70 ml. of purified[2] *n*-dodecane in a 125-ml. erlenmeyer flask fitted with a gas inlet tube at the base, a thermometer, a reflux condenser and a dropping funnel was added 8.2 g. (0.356 g.-atom) of sodium, cut into thin slices, and 18.5 g. (0.0589 mole) of di-*s*-butylmercury. The system was immediately swept out with purified nitrogen. Stirring was accomplished with the aid of an A. H. Thomas Co. magnetic stirrer, and the temperature of the reaction flask was maintained between 20–25° by means of a cold water-bath.

Within ten minutes the mixture became yellow and in 30 minutes had turned brown. After four hours dry carbon dioxide was bubbled through it for one hour. Then water was added cautiously over a four-hour period. The aqueous and hydrocarbon layers were separated and the amalgam removed from the aqueous solution. Upon decomposition with dilute sulfuric acid the amalgam yielded 11.3 g. (0.0563 mole, 95%) of mercury.

After extraction with pentane the aqueous layer was acidified and again extracted with pentane. On removal of the pentane there was obtained 0.5 g. of a brown liquid acid, micro b.p. 182° (uncor.). The *p*-bromophenacyl ester melted at 48–51° and gave no depression of the m.p. when admixed with an authentic specimen of the *p*-bromophenacyl ester of methylethylacetic acid (m.p. 55°).

The acidified aqueous solution was next saturated with sodium chloride and extracted with methyl ethyl ketone. Removal of the solvent gave 1.0 g. of a brown oil which partially crystallized on standing. The crystals were washed with pentane and sublimed at 118–124°. The sublimed crystals melted sharply at 124.5° (methylethylmalonic acid is reported to melt at 121°[8]).

Decomposition of *s*-Butylsodium.—An apparatus similar to that described above was used but so adapted that the evolved gases could be collected over saturated sodium chloride solution. Sodium (0.07 mole) was introduced into the flask and the system swept out with nitrogen. Di-*s*-butylmercury (0.016 mole) was then added through the dropping funnel and the mixture stirred intermittently at room temperature for a period of about eight days. The apparatus was then flushed out with a measured volume of nitrogen and the total collected gases (0.024 mole, exclusive of nitrogen) passed over bromine at −10 to 0° in a brominator similar to that described by Lucas, Dillon and Young.[9] From the loss in gas volume before and after bromination it was estimated that 0.013 mole of butene had been absorbed. The dibromobutane so obtained boiled at 72–73° (42 mm.), n^{25}D 1.5099 (Dillon, Young and Lucas[10] report for *meso*-2,3-dibromobutane, b.p. 72.7–72.9° (50 mm.), n^{25}D 1.5092; for *rac*-2,3-dibromobutene, b.p. 75.6–75.8° (50 mm.), n^{25}D 1.5125). The exit gases from the bromination were freed from bromine (bisulfite), dried and passed into a liquid air trap. From the change in volume it was estimated that 0.004–0.005 mole of gas was condensed by the trap. On cautious warming the condensed liquid was observed to evaporate at −6 to 3° (butane boils at −0.5°[11]).

To the residue in the reaction flask was added pentane and then water. The layers were separated and the amalgam decomposed with dilute sulfuric acid, 0.0154 mole of mercury being obtained. The dried pentane layer was found to distil practically completely as pentane (b.p. 36–37°). No trace of 3,4-dimethylhexane (b.p. 118°[2]) could be detected.

On repetition of the foregoing experiment with 0.17 g.-atom of sodium and 0.017 mole of di-*s*-butylmercury substantially the same results were obtained. Thus, 0.0166 mole of mercury was found to be present in the amalgam and 0.026 mole of gas was evolved which was estimated to contain 0.016 mole of butene.

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[4] A. A. Morton, *et al.*, THIS JOURNAL, **58**, 1697 (1936); **64**, 2240 (1942).

[5] C. S. Marvel and H. O. Calvery, *ibid.*, **45**, 820 (1923).

[6] H. Gilman and R. E. Brown, *ibid.*, **52**, 3314 (1930).

[7] F. C. Whitmore and R. J. Sobatzki, *ibid.*, **55**, 1128 (1933).

[8] A. I. Vogel, *J. Chem. Soc.*, 1478 (1929).

[9] H. J. Lucas, R. T. Dillon and W. G. Young, THIS JOURNAL, **52**, 1949 (1930).

[10] R. T. Dillon, W. G. Young and H. J. Lucas, *ibid.*, **52**, 1953 (1930).

[11] G. Egloff, "Physical Constants of Hydrocarbons," Vol. I, Reinhold Publishing Corp., New York, N. Y., 1939, p. 30.

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Eight-Membered Carbocycles. III. Hydrogenation of Vinylcyclooctatetraene

BY CLIFFORD E. LARRABEE AND L. E. CRAIG

The hydrogenation of a mixture of 1-phenyl-1,3-butadiene and vinylcycloöctatetraene to give a mixture of *n*-butylbenzene, 1-ethylcycloöctene and ethylcycloöctane has been reported previously.[1] It was, at first, thought that the presence of 1-ethylcycloöctene among the products might be due to interruption of the hydrogenation before it was completed. An experiment with a pure sample of vinylcycloöctatetraene showed that this was not true and a series of room-temperature hydrogenations was carried out under a variety of conditions.

Hydrogenation of vinylcycloöctatetraene in glacial acetic acid in the presence of Adams catalyst was found to proceed readily to the point of complete saturation and the formation of ethylcyclooctane. When methanol was used in place of acetic acid, it was found that the hydrogenation

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[1] L. E. Craig and C. E. Larrabee, THIS JOURNAL, **73**, 1191 (1951).