against a saturated calomel electrode and all half-wave potentials were corrected to refer to the latter electrode.

The original runs were made with a solvent consisting of 75% dioxane–25% water, the supporting electrolyte being 0.05*M* tetrabutylammonium chloride. This was the solvent used by von Stackelberg and Stracke.[2] The dioxane was purified by the method of Hess and Frahm.[8] Later 80% ethanol–20% water was found to be a suitable solvent and was considerably more convenient than dioxane. A higher concentration of supporting electrolyte was used with the alcohol solutions, the cell solutions being 0.10*M* in both tetrabutylammonium chloride and tetrabutylammonium hydroxide. Blanks run with these solutions showed that appreciable decomposition of the supporting electrolyte did not occur below about −2.6 volts. The concentration of ketone in all cases was 0.001*M*. A single capillary of Corning Marine barometer tubing was used. The value of $m^{2/3}t^{1/6}$ was 1.63 determined in 80% ethanol with an open circuit, and 1.45 at −2.40 v.

The macroelectrolyses were carried out using a potentiostat of the Lingane-Jones type.[9] A hydrogen-oxygen coulometer was used in the coulometric measurements. The cell, electrodes, and experimental procedures were essentially those recommended by Lingane.[10] In most cases identification of a product was carried out by comparison of its infrared spectrum to that of the authentic compounds.

The samples of III, IV, and V[5] were kindly furnished us by Dr. Charles T. Lester. The samples of polarographically pure tetrabutylammonium hydroxide and chloride were obtained from Southwestern Analytical Chemical Corp. All other organic reagents were Eastman white label products and were used without further purification.

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(8) K. Hess and H. Frahm, *Ber.*, **71**, 2627 (1938).
(9) J. J. Lingane and S. L. Jones, *Anal. Chem.*, **22**, 1169 (1950).
(10) J. J. Lingane, *Electroanalytical Chemistry*, 2nd Ed., Interscience Publishers, Inc., New York, 1958, p. 251.

Alkylation of Some Diacylhydrazines[1]

R. L. HINMAN[2] AND RICHARD J. LANDBORG

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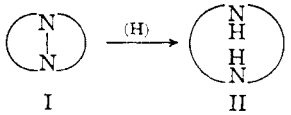
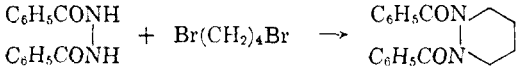
This report summarizes the preliminary work in a program aimed at the synthesis of bicyclic hydrazines (I) and conversion of the latter by hydrogenolysis to large ring diamines (II). The recent report[3] of the successful completion of a similar



I II

study has prompted us to terminate our own work n this area and to submit a brief account of experiments related to the syntheses of the precursors of the bicyclic hydrazines (I).

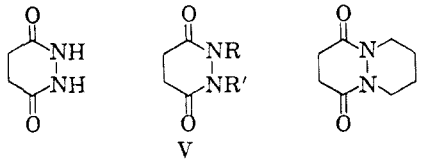
Like Stetter and Spangenberger we were unable to effect the alkylation of 1,2-dibenzoylhydrazine with trimethylene bromide. We found, however, that 1,2-dibenzoylhydrazine and tetramethylene bromide in basic solution yield 1,2-dibenzoylhexahydropyridazine (III). The structure of III was established by its carbon, hydrogen analysis,



III

its insolubility in basic solution, and its melting point.[4] Similar results have been obtained by using 1,2-diacetyl- and 1,2-diisobutyrylhydrazine.[3]

Alkylation of cyclic succinhydrazide (IV) by dimethyl sulfate in basic solution yielded 1,2-dimethylhexahydropyridazine-3,6-dione (Va), previously prepared by the hydrogenation of *N,N'*-dimethylmaleic hydrazide.[5] Alkylation of IV with



IV V VI

a. R = R' = CH_3
b. R = H; R' = C_2H_5

ethyl iodide, however, yielded a product (Vb) bearing only one ethyl group. Assignment of structure Vb to the product is supported by the C, H analysis, the decreased melting point of the product relative to that of the starting material,[4] and the fact that the product could be extracted from acidic solution, but not from basic solution, in accord with the acidic properties of acylhydrazines containing the –CONH– group. Attempts to alkylate IV with tetramethylene bromide yielded a product, presumed to be VI. Although the product could not be purified sufficiently to yield satisfactory analytical results, the melting point (179–181°) agrees well with that (179–180°) reported[3] for VI, which was prepared from piperidazine and succinic anhydride. Extraction of the product from basic solution, and the decrease in the melting point relative to the starting material[4] is additional evidence in support of structure VI.

The cyclic succinhydrazide (IV) was prepared by catalytic hydrogenation of maleic hydrazide.[6] However, consistently successful reductions were obtained only if the latter compound was refluxed with a small quantity of Raney nickel before use.

(1) Taken from the M.S. thesis of R. J. Landborg, State University of Iowa, August 1957.
(2) Present address: Union Carbide Research Institute, 32 Depot Plaza, White Plains, N. Y.
(3) H. Stetter and H. Spangenberger, *Ber.*, **91**, 1982 (1958).
(4) A decrease in m.p. usually accompanies substitution of an alkyl group for the peptide hydrogen of an acylhydrazine, R. L. Hinman and M. C. Flores, *J. Org. Chem.*, **24**, 660 (1959).
(5) K. Eichenberger, A. Staehelin, and J. Druey, *Helv. Chim. Acta*, **37**, 837 (1954).
(6) H. Feuer, G. B. Bachman, and E. H. White, *J. Am. Chem. Soc.*, **73**, 4716 (1951).

Attempts to prepare the cyclic succinhydrazide by alternative methods; such as the reaction of diethyl succinate and hydrazine at high dilution, intramolecular cyclization of succindihydrazide in refluxing butyl cellosolve, and the reaction of hydrazine with *N*-benzylsuccinimide were unsuccessful.

EXPERIMENTAL[7]

1,2-Dibenzoylhexahydropyridazine. A solution of 1.8 g. (0.008 mole) of tetramethylene bromide in 30 ml. of absolute alcohol was added slowly with stirring to a refluxing solution of 2 g. (0.008 mole) of dibenzoylhydrazine[8] in 100 ml. of 60% ethanol. Sufficient concentrated sodium hydroxide was added throughout the reaction to maintain a *p*H of 8–9. After 8 hr. the alcohol was removed by distillation during which water was added to replace the alcohol. The aqueous solution was extracted several times with chlorofrom and the combined extracts dried over anhydrous sodium sulfate. After removal of the solvent by evaporation, the residue (0.5 g., 20%) consisted of white crystals melting at 124–127°. An analytical sample was prepared by recrystallization from a mixture of hexane and chloroform followed by 2 sublimations. The melting point of the hygroscopic crystals was raised to 130°.

Anal. Calcd. for $C_{18}H_{18}N_2O_2$: C, 73.46; H, 6.15; N, 9.51. Found: C, 73.06; H, 6.08; N, 8.99.

Only starting material was isolated from the reaction of 1,2-dibenzoylhydrazine and trimethylene bromide under similar conditions.

Hexahydropyridazine-3,6-dione. This compound was prepared by catalytic reduction of maleic hydrazide by a modification of the method of Feuer, Bachman, and White.[6] Practical grade maleic hydrazide was recrystallized from water, refluxed with 4% of its weight of Raney nickel in water, and recrystallized again from water. By use of this procedure the amount of platinum oxide catalyst necessary for the reduction of maleic hydrazide could be reduced to half that previously required, the reaction time shortened, and the reductions made consistently successful. The product, which was obtained in 70–80% yield, consisted of white needles, m.p. 277° (lit.[6] m.p. 277–278°). High pressure reductions using Raney nickel catalyst gave starting material or a mixture of products. Only starting material was isolated from the reduction at room temperature using aluminum amalgam.[6]

1,2-Dimethylhexahhyropyridazine-3,6-dione. A solution of 4.0 g. (0.034 mole) of dimethyl sulfate in 75 ml. of 50% ethanol was added with stirring over a period of 4 hr. to a refluxing solution of 2 g. (0.017 mole) of cyclic succinhydrazide in 60 ml. of 50% alcohol. The reaction mixture was maintained at a *p*H of 8–9 by the addition of small amounts of concentrated aqueous sodium hydroxide. At the end of the reaction time the alcohol was removed by distillation during which water was added to replace the alcohol. The remaining aqueous solution was extracted several times with chloroform and the combined extracts were dried over anhydrous sodium sulfate. The average yield of crude product after the evaporation of the solvent was 0.4 g. (16%). After recrystallization from a mixture of hexane and chloroform and 2 sublimations, the melting point of the purified compound was 104–105° (lit.[5] m.p. 104–105°). The compound was highly hygroscopic.

Alkylation of hexahydropyridazine-3,6-dione with ethyl iodide. The above alkylation was carried out substituting 5.3 g. (0.034 mole) of ethyl iodide in 30 ml. of ethanol for the dimethyl sulfate solution. After recrystallization from a mixture of hexane and chloroform and 2 sublimations, 0.3 g. (12%) of white crystals melting at 140–142° was obtained. The compound analyzed for 1-ethylhexahydropyridazine-3,6-dione.

Anal. Calcd. for $C_6H_{10}N_2O_2$: C, 50.70; H, 7.04. Found: C, 50.66; H, 7.10.

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(7) Melting points are uncorrected.

(8) H. H. Hatt, *Org. Syntheses*, **Coll. Vol. II**, 208 (1943).

Polyphosphoric Acid–Catalyzed Reaction of Anisole with γ-Butyrolactone

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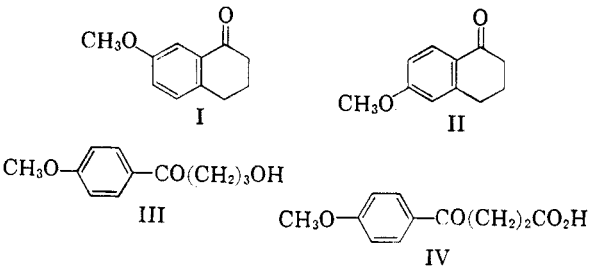
The reaction of γ-substituted-γ-butyrolactones with benzene and alkyl-substituted benzenes in the presence of aluminum chloride has served to produce γ-aryl-γ-substituted butyric acids.[1,2] The comparable reaction of benzene with γ-butyrolactone in the presence of excess aluminum chloride afforded α-tetralone in one step.[3] These observations suggested that 7- (or 6-) alkoxy-1-tetralones might be prepared directly by the reaction of alkoxybenzenes with γ-butyrolactone in the presence of polyphosphoric acid.[4,5]

The reaction of anisole with γ-butyrolactone in the presence of polyphosphoric acid was found to yield neither of the expected tetralones I or II, but rather a hydroxy ketone which has infrared and ultraviolet spectra compatible with structure III. This structure was confirmed by oxidation of the product to form the keto acid IV.



EXPERIMENTAL[6]

γ-Hydroxy-p-methoxybutyrophenone (III). A mixture of 6.14 g. (0.0568 mole) of anisole and 4.876 g. (0.0568 mole) of

(1) J. F. Eijkman, *Chem. Weekblad*, **1**, 421 (1904).

(2) D. D. Phillips, *J. Am. Chem. Soc.*, **77**, 3658 (1955).

(3) C. E. Olson and A. R. Bader, *Org. Syntheses*, **35**, 95 (1955).

(4) For a review of cyclizations effected in the presence of polyphosphoric acid, see F. D. Popp and W. E. McEwen, *Chem. Revs.*, **58**, 321 (1958).

(5) A successful intermolecular acylation of anisole reported by N. C. Deno and H. Chafetz [*J. Org. Chem.*, **19**, 2015 (1954)] may have involved a γ,γ-disubstituted butyrolactone as an intermediate.