analysis shown in Fig. 2 indicates that the latter compounds also differ sufficiently among themselves to permit simple *p*H and ionic strength adjustments to accomplish the separation of each component (*cf.* Carter and Cohn[11]).

Discussion

Since the elution position of glucose-1-phosphate is unaffected by moderate amounts of borate ion, it would appear that this compound does not form a borate complex. This observation is in agreement with the principles discussed in the studies on the ion-exchange behavior of the sugar–borate complexes and with the conductivity studies of sugar derivatives carried out in solutions of boric acid by MacPherson and Percival[21] which indicate that the presence of a phosphate group on carbon atom number one in glucose eliminates the possibility of a strongly ionized borate complex being formed.

From the behavior of neutral sugars in borate solutions, it was concluded[13] that the ion-exchange affinities of borate diols formed from furanose structures were greater than those formed from pyranose structures. A separation of these two borate diols of one given sugar was not obtained, presumably due to the equilibrium which exists between the two forms. In the present studies, this conclusion is confirmed. Glucose-6-phosphate can form a borate complex from either its pyranose or furanose structure, while the ring form of fructose-6-phosphate and ribose-5-phosphate can only be of the furanose type. These latter two sugar phosphates exhibit a very strong affinity for the exchanger when only small amounts of borate ion (about 0.0005 M) are included in the ammonium chloride–ammonium hydroxide eluting solutions. The affinity of glucose-6-phosphate remains unchanged unless the borate ion concentration is increased at least twentyfold (about 0.01 M). It is most probable, as assumed for the sugars, that an equilibrium exists between the two forms of the borate complex of glucose-6-phosphate, which allows less time for the borate complex of the furanose form to make contact with the exchanger. Therefore, if interconversion is possible in a sugar phosphate, less affinity for the exchanger is to be expected than where only a furanose ring form can exist.

The elution order of the adenosine derivatives has already been established.[11] After removal of the monophosphorylated sugars from the exchanger, the elution system reported here differs only slightly in that ADP is eluted at a lower chloride ion concentration allowing elution of fructose-1,6-diphosphate between ADP and ATP. The presence of two ionizable groups in fructose-1-diphosphate and 2-PGA easily explains the strong affinity of these compounds for the exchanger.

Acknowledgment.—The authors wish to express appreciation to Dr. G. R. Noggle for performing the paper chromatographic analyses on the sugar phosphates isolated by the ion-exchange columns during these experiments.

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[CONTRIBUTION NO. 292 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY]

Alicyclic Diamines. Preparation of Bis-(4-aminocyclohexyl)-methane

BY A. E. BARKDOLL, D. C. ENGLAND, H. W. GRAY, W. KIRK, JR., AND G. M. WHITMAN

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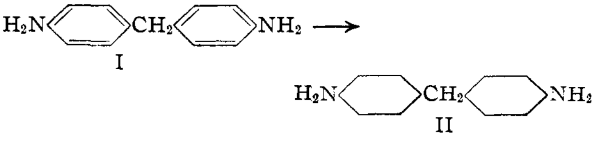
While the hydrogenation of simple aromatic monoamines to the corresponding alicyclic amines can be accomplished with common catalysts such as Raney nickel, the hydrogenation of more complex aromatic diamines such as bis-(4-aminophenyl)-methane (I) to bis-(4-aminocyclohexyl)-methane (II) presents a more difficult problem. Accordingly, the application of a number of catalysts to the hydrogenation of I to II has been studied, with the finding that ruthenium dioxide is a very effective catalyst for this hydrogenation. Also, German reports of the activity of a mixture of cobaltic oxide–calcium oxide–sodium carbonate as a catalyst for the hydrogenation of I to II have been confirmed, and some observations have been made on the role played by the various components of this catalyst.

Numerous catalysts and techniques[1] have been described for the hydrogenation of relatively simple monocyclic aromatic amines to the corresponding alicyclic amines. The use of certain of these catalysts which require an acid medium for successful operation is accompanied by a corrosion problem in metal equipment, and necessitates recovery of the product from the acid medium. Also, the hydrogenation of aromatic amines in glacial acetic acid solution with platinum oxide catalyst, as exemplified by the reduction of benzidine,[2] frequently yields ammonia and condensation products, in addition to the desired product. Other catalysts, such as Raney cobalt, when applied to relatively complex diamines such as bis-(4-aminophenyl)-methane (I) are reported to be ineffective.[3]



Recently, two excellent catalysts for the hy-

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[1] P. Sabatier and J. B. Senderens, *Compt. rend.*, **138**, 457 (1904); R. Willstätter and D. Hatt, *Ber.*, **45**, 1471 (1912); A. Skita and W. Berendt, *ibid.*, **52**, 1519 (1919); G. S. Hiers and R. Adams, *ibid.*, **59**, 162 (1926); H. Heckel and R. Adams, THIS JOURNAL, **47**, 1712 (1925); G. S. Hiers and R. Adams, *ibid.*, **49**, 1099 (1927); H. Adkins and H. I. Cramer, *ibid.*, **52**, 4349 (1930).

[2] F. Balas and P. Sěvcěnko, *Collection Czechoslov. Chem. Commun.*, **3**, 171 (1931); C. A., **25**, 2990 (1931).

[3] O. P. B. Report, PB-742 (1941) "4,4'-Diaminodicyclohexylmethane."

TABLE I

HYDROGENATION OF BIS-(4-AMINOPHENYL)-METHANE

Expt. no.	Reactants Catalyst, g.		Amine, g.	Solvent, ml.	Adjuvant, g.	Conditions Temp., °C.	Press., atm.	Time, hr.	Yield diamine, %
1	Co-on-Al$_2$O$_3$[a]	10	49.5	Dioxane 125	NH$_3$ 17	225	200	2.5	0
2	Co-on-Al$_2$O$_3$[a]	10	100			250	950	3.5	0
3	Co-on-Al$_2$O$_3$[a]	5	25	Dioxane 100	NH$_3$ 18	250	950	3	52
4	Raney Ni[b]	5	25	Dioxane 100	NH$_3$ 17	250	915	3	47
5	Raney Ni[b]	5	49.5	Dioxane 125		200	175–200	6.5	0
6	Ruthenium dioxide[c]	2.5	49.5	Dioxane 125		100	100–135	3	79
7	Ruthenium dioxide[c]	2	150			115	133–187	10	61
8	Ruthenium dioxide[c]	1	49.5	Dioxane 50	NH$_3$ 50	120	187	6.5	78
9	Ruthenium dioxide[c]	25	1250	Dioxane 3125		100–120	133–200	4	92
10	Sodium ruthenate-on-carbon[d]	0.84	60	Dioxane 150		200	200	6.3	78
11	Platinum oxide (Adams)	2	39.6	Acetic acid 175		*ca.* 25	2–3	24	23
12	Alkali-promoted cobaltic oxide[e]		100			215	120–220	6	86

[a] The cobalt-on-alumina catalyst was prepared and stabilized according to Example 4, U. S. Patent 2,166,183. [b] Prepared according to the method of Pavlic and Adkins, THIS JOURNAL, **68**, 1471 (1946). [c] This catalyst was purchased from Baker and Company, 113 Astor Street, Newark, N. J. [d] The sodium ruthenate-on-carbon, containing 6.9% ruthenium, was prepared according to Example 5, U. S. Patent 2,606,925. An induction period of about 1.5 hours was observed before hydrogenation began. The catalyst was recovered and reused twice, 59% II being obtained from the last run. [e] The catalyst, described in O. P. B. Report, PB-742 (1941), "4,4-Diaminodicyclohexylmethane," consisted of 10 g. of cobaltic oxide, 15 g. of calcium oxide and 6.5 g. of anhydrous sodium carbonate.

drogenation of aromatic amines to the corresponding alicyclic amines have been reported, namely, (1) ruthenium catalysts[4–6] discovered in this Laboratory and (2) an alkali-promoted cobaltic oxide catalyst developed in Germany.[3,7] Study of these catalysts has indicated them to be effective for the hydrogenation of aromatic amines in general to the corresponding alicyclic amines; however, this paper will be concerned only with the hydrogenation of I to bis-(4-aminocyclohexyl)-methane (II).

Ruthenium Catalysts.—Ruthenium dioxide has been found to catalyze the hydrogenation of I to II in yields as high as 94%. The hydrogenation proceeds at a satisfactory rate in dioxane solution at temperatures of 100–150° and pressures of 1500–3000 lb./sq. in. Ordinarily, 0.5–1.5% of ruthenium in the form of ruthenium dioxide is employed, although satisfactory hydrogenation at 200° has been observed with as little as 0.05% of ruthenium in the form of sodium ruthenate supported on carbon. The active catalyst is probably metallic ruthenium, as suggested by the pyrophoric nature of the recovered catalyst.

Promoted Cobalt Oxide Catalysts.—The calcium oxide-sodium carbonate-cobaltic oxide catalyst developed in Germany,[3,7,8] while not possessing the versatility and effective temperature range of ruthenium, nevertheless is a useful catalyst for the hydrogenation of I to II. A study of this catalyst for the hydrogenation of I in the absence of a solvent has indicated the optimum conditions to be 215° and 3000 lb./sq. in. pressure, II being obtained in yields as high as 86% under these conditions. The catalyst is essentially inactive below 200°. Proper balance of the catalyst ingredients, *i.e.*, 15 parts of calcium hydroxide, 6.5 parts of sodium carbonate and 10 parts of cobaltic oxide per 100 parts of I, the proportions previously reported,[3] is essential for the most efficient utilization of the catalyst. Reduction of the amount of catalyst to one-third of this amount resulted in a lower yield (35%) of II. Omission of both calcium oxide and sodium carbonate resulted in an inactive catalyst.

Other Catalysts.—Results with other cobalt and nickel catalysts are summarized in Table I. These catalysts, which were not so active as the ruthenium and promoted cobaltic oxide catalysts, required higher temperatures, of the order of 225–250°, for appreciable catalytic activity. The addition of anhydrous ammonia, while repressing hydrogenation to some extent, nevertheless decreased deamination and condensation and gave reasonable yields of II.[9] The use of platinum oxide (Adams) catalyst in glacial acetic acid at room temperature and a pressure of 2–3 atmospheres led to the formation of 23% of II, together with considerable polymeric product.

Effect of Catalyst on Isomer Distribution.—It is possible for II to exist in three geometrically isomeric forms, *i.e.*, *cis–cis*, *cis–trans* and *trans–trans* forms.[1] As far as is known, the catalysts and conditions described in this paper invariably lead to a mixture of all three isomers of II. However, the relative amounts of the three isomers formed vary widely, depending on the catalyst and conditions. For example, the use of ruthenium at temperatures of 100–120° results in II having only a relatively small portion of *trans–trans* isomer, the remainder being a mixture of the *cis–cis* and *cis–trans* isomers. Increase in the temperature results in a relatively greater amount of the *trans–trans* isomer being formed.

In the case of the alkali-promoted cobaltic oxide catalyst, the major component is the *trans–trans* isomer, followed by the *cis–trans* isomer, with only a small quantity of the *cis–cis* isomer formed.[8] This may be a characteristic property of the cobalt catalyst, as well as a consequence of the relatively high temperature (*ca.* 215°) required for effective use of the catalyst. Operation at still higher temperatures appears to have little effect on the isomer composition but lowers the yield of II due to formation of deamination products; the catalyst is ineffective at temperatures much below 215°.

Precise characterization of mixtures of the three isomers has not been convenient because of the close correspondence of the physical properties of the isomers and their mixtures. However, a qualitative indication of differences in the isomer composition of the products obtained on hydrogenation has been furnished by refractive index and freezing point. Also, differences in isomer composition of the alicyclic diamine are apparent on preparation of the corresponding adipic acid polyamides. Thus, depending on the isomer content, adipic acid polyamides may vary from transparent, fusible polymers to opaque, fusible or infusible polymers. The two examples shown in Table II are illustrative of diamine isomer mixtures and their corresponding adipic acid polyamides which may be obtained with ruthenium and cobaltic oxide catalysts. It is believed that the *trans–trans*

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(4) G. M. Whitman, U. S. Patent 2,606,924 (1952); G. M. Whitman, U. S. Patent 2,606,925 (1952).

(5) A. E. Barkdoll, C. D. Bell and E. R. Graef, U. S. Patent 2,606,928 (1952).

(6) L. C. Behr, *et al.*, THIS JOURNAL, **68**, 1296 (1946).

(7) B.I.O.S. Final Report No. 1472, Item No. 22 "Some Aspects of Textile Research in Germany," p. 6.

(8) A. E. Barkdoll, H. W. Gray and W. Kirk, Jr., THIS JOURNAL, **73**, 741 (1951).

(9) A. E. Barkdoll and G. M. Whitman, U. S. Patent 2,606,927 (1952).

isomer is responsible for the infusibility of the polyamides prepared from certain of the diamine compositions.[10]

Experimental

Materials.—The dioxane used as solvent in these experiments was purified by refluxing with sodium. In a few cases, the more thorough procedure described by Fieser[11] was employed. No difference in hydrogenation behavior was observed using dioxane purified by the two methods.

TABLE II

Hydrogenation conditions	Catalyst	RuO_2	Co_2O_3
	Temp., °C.	100–120	215
Diamine properties	$n^{25}D$	1.5051	1.5031
	Physical state at room temp.	Sirup	Semi-solid
Adipic acid polyamide properties	Soft. temp., °C.	259	Dec. above 306
	Optical prop.	Translucent	Opaque

Bis-(4-aminophenyl)-methane (I) was either purchased from the Dow Chemical Company or prepared from aniline by a modification of the procedure of Wagner.[12] Purification of I was effected by fractional distillation. In some cases the distilled aromatic diamine was also recrystallized from 95% ethanol or thiophene-free benzene.

Ruthenium dioxide was obtained from Baker and Company, Inc., 113 Astor Street, Newark 5, N. J.

Cobaltic oxide was prepared by calcination of cobaltous nitrate hexahydrate in the presence of air. Commercial samples of cobaltic oxide, C.P. grade, were also found to be satisfactory.

Calcium oxide was prepared by heating reagent grade samples of calcium hydroxide or calcium carbonate in a muffle furnace in air for 24 hr. Optimum temperatures were found to be *ca.* 500° for calcium hydroxide and 750° for calcium carbonate.

Anhydrous sodium carbonate, reagent grade, such as that supplied by Mallinckrodt Chemical Works, was used.

Equipment.—Unless otherwise noted, the hydrogenations were carried out in pressure vessels of one or the other of the following two general types: Type A, vessels of 400 ml. total capacity, heated either externally or internally, which were shaken to provide agitation; Type B, small autoclaves of 1–2 gallon capacity which were provided with a stirrer, and heating and cooling facilities.

Hydrogenation Procedure.—The aromatic diamine, solvent and catalyst were added to the pressure vessel, which was then closed and maintained at the desired conditions of temperature and hydrogen pressure with agitation for the desired time. In the case of autoclave runs, several pressurings with hydrogen to *ca.* 200 lb./sq. in., followed by purging, preceded the hydrogenation. For runs to which anhydrous ammonia was added, the pressure vessel was cooled in a mixture of Dry Ice and acetone and evacuated; ammonia was then distilled into the pressure vessel. After the reaction, the vessel was cooled and the contents were discharged, methanol being used to rinse the vessel. The reaction product was filtered through a bed of activated carbon to remove the catalyst, suitable precautions being taken in view of the pyrophoric nature of the catalyst. After removal of the solvent, the product was isolated by distillation.

The general procedure is illustrated by the following experiment in which ruthenium dioxide was used as the catalyst. A mixture of 1250 g. (6.3 moles) of I, 3125 ml. of dioxane and 25 g. of ruthenium dioxide was charged into a 1-gallon autoclave. The vessel was repeatedly pressured to 200 lb./sq. in. with hydrogen and purged to remove air. The mixture was hydrogenated for 4 hours at 100–120° and 166–200 atm. pressure. The reaction mixture was cooled and rinsed from the autoclave with methanol; 15 g. of Darco was added to the reaction mixture, and the catalyst was filtered by suction through a buchner funnel precoated with 15 g. of Darco. The solvent was removed by distillation at atmospheric pressure and the dark liquid residue of crude diamine was fractionated under reduced pressure to yield 1223 g. (92%) of II boiling at 120° (0.8 mm.) –128° (1.2 mm.); $n^{25}D$ 1.5051; neut. equiv., 105.1 (calcd. 105.2).

Characterization of Diamine Mixtures.—The freezing point determinations on the diamine mixtures were carried out in a small vacuum-jacketed test-tube by permitting the diamine sample to cool slowly at a rate of about 1° per minute. The samples were seeded to initiate crystallization. The freezing point was taken as the point at which the temperature remained constant for several minutes.

The adipic acid polyamides were prepared in the conventional manner[10,13] with precautions being taken to ensure that no appreciable fractionation of isomers occurred during precipitation of the adipic acid salts.

Discussion of Experimental Data

Ruthenium dioxide has been found to be an excellent catalyst for the hydrogenation of I to II, yields as high as 92% II being observed with 2% of RuO_2 at 100–120° and 133–200 atmospheres in dioxane solvent (Expt. 9, Table I). This catalyst is also effective in the absence of a solvent (Expt. 7) or in the presence of anhydrous ammonia (Expt. 8), although the rate of hydrogenation is decreased in these cases. Satisfactory hydrogenation has been observed at temperatures as low as 100°, although 120° gives better results from the standpoint of rate of hydrogenation, using 2% of ruthenium dioxide. Hydrogenation of I to II in 78% yield has been observed with as little as 0.1% of ruthenium in the form of sodium ruthenate-on-carbon, although a temperature of 200° was required.

The effect of the various constituents of the promoted cobaltic oxide catalyst was determined by varying one component while maintaining constant proportions of the other components. Commerical samples of cobaltic oxide, used in conjunction with suitable samples of calcium oxide and sodium carbonate were found to give yields of II as high as 86% (Expt. 12, Table I). However, on omission of the calcium oxide and sodium carbonate, the yield of II fell to zero. If the cobaltic oxide were prereduced to metallic cobalt in hydrogen at 400° before incorporation of the other catalyst ingredients, it was no longer active for hydrogenation of I. Loss of activity also occurred if the complete catalyst mixture was reduced at 400° in hydrogen before use. It has been asserted that the catalyst cannot be reused.[4] However, we have found that it is possible to use the catalyst at least three times, provided air is carefully excluded from the pyrophoric catalyst during recovery. However, the yield of II fell to 44% for the third use from an initial value of 81%.

Samples of oxides of cobalt were prepared by pyrolysis of cobaltous nitrate hexahydrate at various temperatures and their catalytic properties correlated with cobalt content and specific surface area.[14] Heating periods of 15 to 24 hours were found to be satisfactory. It was found that catalysts essentially equivalent in quality were obtained using pyrolysis temperatures ranging from 200° to 750°, although specific surface area fell

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[10] A. E. Barkdoll, H. W. Gray, W. Kirk, Jr., D. C. Pease and R. S. Schreiber, contrib. No. 297, THIS JOURNAL, **75**, 1238 (1953).

[11] L. F. Fieser, "Experiments in Organic Chemistry," Second Edition, D. C. Heath and Co., New York, N. Y., 1941, p. 368.

[12] E. C. Wagner, THIS JOURNAL, **56**, 1944 (1934).

[13] E. K. Bolton and W. Kirk, Jr., U. S. Patent 2,512,606 (June 27' 1950).

[14] S. Brunauer, P. H. Emmett and E. Teller, THIS JOURNAL, **60**, 309 (1938); P. H. Emmett and T. De Witt, *Ind. Eng. Chem., Anal. Ed.*, **13**, 28 (1941); P. H. Emmett, "New Method for Particle Size Determination in the Subsieve Range," ASTM Spring Meeting, Washington, Mar. 4, 1941.

off progressively as the pyrolysis temperature was raised. For example, the catalyst prepared at 200° had a specific surface area of 9.3 sq.m./g. and catalyzed the formation of the alicyclic diamine in 80% yield; the catalyst prepared at 750° also gave alicyclic diamine in 80% yield, although the specific surface area fell to 1.5 sq.m./g. X-Ray examination of the samples prepared at temperatures up to 750° indicated all to be Co_3O_4. However, a diffraction pattern characteristic of CoO was observed with oxide which had been prepared by pyrolysis at 1000°. The specific surface area of this catalyst, which yielded only 26% diamine, had dropped to 0.1 sq.m./g. These observations are confirmed by the work of Natta and Strada,[15] who have identified the three oxides of cobalt, *viz.*, Co_2O_3, Co_3O_4 and CoO, by X-ray diffraction, and found that Co_2O_3 could not be prepared by pyrolysis of cobaltous nitrate hexahydrate.

The presence of calcium oxide is essential for catalytic activity. However, other factors being equal, the promoter activity of calcium oxide, as well as its specific surface area, varies widely and depends to a considerable degree on the temperature used for calcination of calcium hydroxide or calcium carbonate to calcium oxide. For example, calcium oxide prepared by calcination of calcium hydroxide at 500° for 24 hours had a surface area of 22.8 sq.m./g. This sample of calcium oxide when used in conjunction with cobaltic oxide, but without sodium carbonate, promoted the formation of II in 55% yield, while the remainder of the product was accounted for by deamination products. Calcium oxide with a surface area of 6.1 sq.m./g., which was prepared by calcination of calcium hydroxide at 750° for 24 hr. under similar conditions, promoted the formation of II in only 41% yield, together with 46% of 4-(*p*-aminobenzyl)-cyclohexylamine and 13% of deamination products. The presence of sodium carbonate in the catalyst appeared to repress side reactions such as deamination, and thus led to higher yields of II. For example, the use of sodium carbonate with cobaltic oxide and calcium oxide having a surface area of 22.8 sq.m./g. resulted in the formation of II in 74% yield, in contrast to a yield of 55% without added sodium carbonate.

So-called "dead-burnt" lime,[16] obtained at temperatures of the order of 1000° and higher, is characterized by a lack of reactivity toward water. We have found that this type of lime is also characterized by a relatively low surface area and by little or no promoter activity.

Cobalt-on-alumina catalyzed the formation of II in 52% yield by operation at a pressure of 950 atmospheres and 250° in the presence of an 8-fold mole excess of anhydrous ammonia (Expt. 3), although hydrogenation was completely repressed by ammonia at lower temperatures and pressures (Expt. 1). Raney nickel was completely ineffective in the absence of ammonia at 200° and 200 atmospheres (Expt. 5), although 47% yield of II was obtained by hydrogenation at 250° and 915 atmospheres in the presence of anhydrous ammonia (Expt. 4).

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[15] G. Natta and M. Strada, *Gazz. chim. ital.*, **58**, 419 (1928).

[16] N. V. S. Knibbs, "Lime and Magnesia," Ernest Benn, Ltd., London, 1924, p. 99.

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, SCHOOL OF MEDICINE, LAVAL UNIVERSITY]

A New Synthetic Approach to the Morphine Structure

BY B. BELLEAU[1]

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The spiroketone, 2,2-tetramethylene-1-tetralone, was converted to 1,2,3,4,9,10-hexahydrophenanthrene by Wagner rearrangement of the intermediate alcohol. Rearrangement of the methylmagnesium iodide addition product of the spiroketone gave only the product of normal dehydration. On the other hand, condensation of the starting ketone with methyl bromoacetate afforded a substance which smoothly underwent Wagner rearrangement to yield a hydrophenanthroid lactone which, after lithium aluminum hydride reduction followed by dehydration, catalytic hydrogenation, reaction with phosphorus tribromide and subsequent reaction with dimethylamine, was successfully converted to the dihydrodesbase of N-methylisomorphinane. Possible reaction mechanisms involved in the formation of the various intermediates are briefly presented.

The elaboration of the ring system characteristic of the morphine alkaloids has presented numerous difficulties. The extensive literature in this field has been reviewed by Stern[2] and several publications have appeared subsequently.[3] Because of the brilliant culmination of Gates' approach in the total synthesis of morphine,[4] it seemed desirable to report our work on a completely new approach to the morphine structure. We have succeeded in synthesizing the dihydrodesbase obtained by Gates and collaborators[5] from N-methylisomorphinane.

The spiroketone, 2,2-tetramethylene-1-tetralone (I), is theoretically a suitable precursor for an angularly substituted hydrophenanthrene related to naturally occurring products. This ketone was

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[5] M. Gates, R. B. Woodward, W. F. Newhall and R. Künzli, *ibid.*, **72**, 1141 (1950).