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Summary

1. A new route to derivatives of diphenyl-

ethane related to materials occurring naturally is demonstrated.

2. 4- β -Phenethylindane is synthesized as representing the ring system for the proposed structure for calciferol and tachysterol.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A Modification of the Clemmensen Method of Reduction¹

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While a great many compounds containing the carbonyl group can be reduced by the method of Clemmensen,² the results sometimes leave much to be desired. Substances which neither dissolve appreciably in the acid mixture nor melt at the boiling temperature usually present difficulties and a number of readily available β -aroylpropionic acids which are of use in the synthesis of polynuclear hydrocarbons are of this type. Thus Fieser and Peters³ observed that β -3-acenaphthoylpropionic acid is but little affected by prolonged boiling with hydrochloric acid and amalgamated zinc, Haworth and Mavin⁴ found β -1-methyl-4-naphthoylpropionic acid to be unusually resistant to reduction, and Cook and Hewett⁵ were unable to reduce β -1-pyrenoylpropionic acid by any of the usual modifications in the original procedure of Clemmensen. Although the addition of a miscible solvent such as alcohol, acetic acid, or dioxane facilitates the reduction of certain ketonic compounds (ketocholanic acids, hydrindones), this leads in the above cases only to resinification. The keto acid appears to undergo polymolecular reduction or condensation at the surface of the metal with the formation of a gummy, insoluble coating which obstructs the normal functioning of the zinc.

It was found by Fieser and Peters³ and by Haworth and Mavin⁴ that the reduction of the above two keto acids can be accomplished by the use of the lower-melting esters, but the yield in the first case was only 40% and the process was tedious. After repeating Fieser and Peters' experiments with the same results it was found that

when toluene was added in quantity sufficient to retain the ester in a clear surface layer the yield of the pure reduction product rose to 60% and the process was greatly simplified. The surface of the metal remained clean and bright throughout the reaction and the product was easily isolated from the toluene layer. Attempts to reduce free β -3-acenaphthoylpropionic acid in the presence of toluene were successful only when a small amount of acetic acid was used to provide the required, slight concentration of the keto acid in the aqueous layer. The toluene probably is beneficial partly because it keeps the otherwise undissolved material out of contact with the metal and partly because in the two-phase system the reduction occurs at such a high dilution that polymolecular reactions are largely inhibited.⁶

Various fellow workers engaged in synthetic experiments in this Laboratory kindly cooperated in testing the toluene method, and the yields of purified products, usually checked in two or more experiments, are summarized in Table I. The author is indebted to Mr. C. K. Bradsher, Mr. J. T. Dunn, Mrs. L. F. Fieser, Dr. E. B. Hershberg, Mr. H. L. Holmes, Mr. W. C. Lothrop, Dr. M. S. Newman and Mr. C. C. Price for permission to report their results. The β -aroylpropionic acids investigated were invariably reduced more satisfactorily in the presence of toluene than without it, and two acids could be reduced in this way but not by the usual procedure. With β -1-pyrenoylpropionic acid, however, the results were negative both with and without toluene. The modification seems definitely advantageous with compounds containing methoxyl groups, for the difficulties frequently experienced are at least mini-

(6) Lewis, Ramage and Robinson [*ibid.*, 1414 (1935)] used anisole in two Clemmensen reductions but gave no results by the usual procedure for comparison.

(1) Paper prepared by L. F. Fieser.

(2) Clemmensen, (a) *Ber.*, **46**, 1838 (1913); (b) **47**, 51, 681 (1914).

(3) Fieser and Peters, *THIS JOURNAL*, **54**, 4374 (1932).

(4) Haworth and Mavin, *J. Chem. Soc.*, 2720 (1932).

(5) Cook and Hewett, *ibid.*, 398 (1933).

TABLE I
 COMPARISON OF YIELDS

Reduction of	Clemmensen's procedure		Yield, %	Modified procedure	
	Yield, %	Experimenter		M. p., ° C.	Experimenter
β -Benzoylpropionic acid	72-78 ^a	E.L.M.	90	46-48	E.L.M.
β - <i>p</i> -Toluypropionic acid	88 ^a	J.T.D.	92	61-62	J.T.D.
β - <i>m</i> -Toluypropionic acid	84	35-36	J.T.D.
β - <i>p</i> - <i>t</i> -Butylbenzoylpropionic acid	72	57-60	C.C.P.
β -1-Naphthoylpropionic acid	86	109	M.F.
β -2-Naphthoylpropionic acid	91	94-96	E.L.M.
β -3-Acenaphthoylpropionic acid	0	Ref. 3	50 ^b	147-148	E.L.M.
Methyl ester	36-47	Ref. 3	60	147-148	E.L.M.
β - <i>t</i> -Butylnaphthoylpropionic acid	78 ^{b,c}	...	C.C.P.
β -3-Methoxybenzoylpropionic acid	15	Ref. 7	25-60	45-47	E.L.M.
β -4-Methoxybenzoylpropionic acid	?	Ref. 8	85	60-61	E.B.H.
β -3-Methoxy-4-methylbenzoylpropionic acid	86	70-71	E.L.M.
β -3,4-Dimethoxybenzoylpropionic acid	?	Ref. 9	80 ^{b,d}	61-62	H.L.H.
β -4-Methoxy-1-naphthoylpropionic acid	43	E.B.H.	53 ^b	129-130	E.L.M.
β -2,5-Dimethyl-4-methoxybenzoylpropionic acid	92	Ref. 10	97	98	W.C.L.
5-Methoxy-6-methylhydrindone-1	85 ^e	...	W.C.L.
1-Benzoylnaphthalene	63	C.K.B.	70	58-59	C.K.B.
β -Naphthyl methyl ketone	52 ^f	...	M.S.N.
1-Benzoyl-4-methoxynaphthalene	0	C.K.B.	30 ^b	82-83	E.L.M.
γ -Phenylbutyrolactone	81	46-48	E.L.M.

^a Following the procedure of "Organic Syntheses," Vol. XV, 1935, p. 64. ^b Acetic acid was added to the reaction mixture. ^c Isolated as the ester; b. p. 185-187° at 6 mm. ^d Four 100-g. portions were reduced and the products combined for purification. The heating was continued in this case for forty-one hours; in earlier reductions continued for only twenty to twenty-two hours the yield was poorer by 10-15%. ^e To complete the reduction it was necessary to submit the crude product to further reaction with no added toluene. ^f B. p. 122-125° at 14 mm.

mized. With neutral ketones of very slight water-solubility it is sometimes difficult to effect complete reduction using toluene, and in the case of hydrindones it probably is better to use a water-miscible solvent.

γ -*m*-Methoxyphenylbutyric acid, a useful intermediate in synthesis, has been prepared from *m*-methoxybenzoyl chloride in about 2% yield in a two-step process involving a Clemmensen reduction⁷ and from *m*-methoxybenzaldehyde in eight steps in about 35% yield.¹¹ A third method was tried in the present work but found unsatisfactory. β -*m*-Methoxybenzoylpropionic acid was obtained fairly satisfactorily from β -benzoylpropionic acid through the *m*-nitro compound, but, although on a small scale the Clemmensen reduction in the presence of toluene seemed promising (60% yield) in comparison with Thompson's results,⁷ on a larger scale a resinous oil separated from the toluene layer, the product was difficult to purify, and the yield was poor.^{11a} In

(7) Thompson, *J. Chem. Soc.*, 2314 (1932).

(8) Krollpfeiffer and Schäfer, *Ber.*, 56, 630 (1923).

(9) Haworth and Mavin, *J. Chem. Soc.*, 1486 (1932).

(10) Clemo, Haworth and Walton, *ibid.*, 2381 (1929).

(11) Robinson and Schlittler, *ibid.*, 1288 (1935).

(11a) In a paper which has come to our hands as the present communication is going to press, Chuang and Huang, *Ber.*, 69, 1505 (1936), have described the same process for the preparation of γ -*m*-methoxyphenylbutyric acid. The procedures for carrying out the

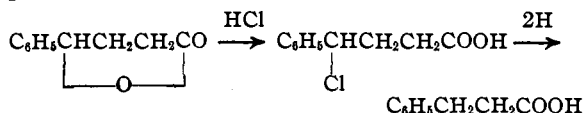
contrast to this experience β -3-methoxy-4-methylbenzoylpropionic acid was prepared easily from β -*p*-toluypropionic acid through the nitro compound and there was no difficulty in effecting the reduction on either a small or large scale, γ -3-methoxy-4-methylphenylbutyric acid being obtained in an over-all yield of 35%. The 3,4-dimethoxy compound (Table I) is also reduced smoothly, and it appears that the abnormal side reaction noted in one case is inhibited by a substituent in the position ortho to the methoxyl and para to the group undergoing reduction.

Turning to another type of reaction, it was found that anthracene and β -methylantracene can be obtained in excellent yield and high purity by the reduction of the anthrones with zinc dust

various steps differ in some details but the results are much the same up to the Clemmensen reduction. Regarding the final step we feel that Chuang and Huang have not adequately demonstrated that the reaction proceeds as well as their statements imply, for they report a yield (87%) only for the crude, alkali-soluble fraction remaining after evaporation of the ether (14-g. run). Martin's yield (60%) for 3-5 g. runs refers to material that had been re-methylated, distilled and obtained as a solid, m. p. 45-47°. It is the general experience in this Laboratory that methoxy compounds invariably are demethylated to some extent even when using toluene, and we found that the resinous material which appeared when operating with moderately large amounts is alkali-soluble and cannot be removed effectively except by distillation. In view of the irregular and generally unsatisfactory results obtained repeatedly by both Martin and Hershberg, we do not share the favorable opinion of the method expressed by the Chinese investigators.—L. F. FISHER.

and sodium hydroxide in the presence of toluene. The process is simpler and more convenient than the usual one.

An incidental observation having some bearing on the mechanism of the Clemmensen reaction is that γ -phenylbutyrolactone gives about as good a yield of γ -phenylbutyric acid as does β -benzoylpropionic acid. Clearly it is not the lactone itself which combines with hydrogen, for the carboxyl group could not then appear in unmodified form, and it may be inferred that the lactone ring first opens with the formation of either the γ -hydroxy acid or the γ -chloro acid and that it is one or the other of these substances which suffers reduction. The chloro compound probably is formed in preponderant amount:



Possibly the reduction of a carbonyl compound with zinc and hydrochloric acid normally proceeds through the alcohol and the chloride. The idea is supported to some extent by the observation that both benzyl alcohol and benzyl chloride, like benzaldehyde,^{2a,12} yield a certain amount of toluene on reduction with zinc and hydrochloric acid. Benzhydrol,¹² triphenylcarbinol¹³ and triphenylbromomethane¹³ have been similarly reduced to the hydrocarbons, but these perhaps are special cases. On the other hand, there have been some reports of the failure to reduce primary^{2b} and secondary alcohols, the most striking example being in the bile acid series. For the conversion of a hydroxycholanolic acid into a cholanic acid the standard method is to oxidize the substance to a ketone and then apply the Clemmensen reaction, for the hydroxy acid usually is converted only into resinous products when treated directly with zinc and acid.¹⁴ Although this would seem to indicate that the alcoholic compound is not an intermediate in the reduction of the ketone, the direct replacement of a hydroxyl group by hydrogen, however rare, has been observed in at least one case (3-hydroxy-12-ketocholanolic acid).¹⁴ Possibly the poor result obtained with a hydroxycholanolic acid is due not to the failure of the substance to undergo reduction but to the occurrence of side reactions, such as dehydration, when the alcoholic compound is present from the start in high concen-

tration. That the carbonyl compound gives a better result may be because the alcohol is never present in large amounts but is rapidly removed from the destructive influence of the acid by reduction, either as such or through the chloride. Possibly it is merely because the di- and tri-aryl carbinols are not subject to dehydration that the direct reduction presents no difficulties.

Experimental Part

Modified Clemmensen Method

General Procedure.—It was found that the time allowed for amalgamating the zinc can be shortened and equally active material obtained by shaking for five minutes a mixture of 100 g. of mossy zinc, 10 g. of mercuric chloride, 5 cc. of concentrated hydrochloric acid and 150 cc. of water. The solution was decanted and the other reagents were added in order as follows: 75 cc. of water, 175 cc. of concentrated hydrochloric acid, 100 cc. of toluene and 50 g. of the carbonyl compound to be reduced. In the case of substances very sparingly soluble in water a small amount (3–5 cc.) of glacial acetic acid was added. The mixture was refluxed briskly for twenty-four hours, three 50-cc. portions of concentrated hydrochloric acid being added at intervals of about six hours. Although this treatment usually is sufficient to complete the reduction, further heating of the reaction mixture with the addition of fresh acid does no harm and in some of the experiments there were indications that the yield is increased slightly by extending the refluxing period.

In the preparation of γ -phenylbutyric acid, its homologs, and other low-melting substances readily soluble in toluene the reaction mixture was cooled to room temperature, the toluene layer was separated and the aqueous layer was diluted and extracted with ether. After removing the solvent from the combined extracts the product was distilled in vacuum, giving material which ordinarily required no further purification. In working up the reaction mixtures from methoxylated keto acids the procedure was modified as follows to provide for the recovery of demethylated material. The combined solution in toluene and ether was mixed with an excess of dilute alkali, the solvent was removed by steam distillation, and after cooling the alkaline solution to about 80° an excess of dimethyl sulfate (20–25 cc.) was added, keeping the solution alkaline. In case the solution tended to darken, sodium hydrosulfite was added. Any ester which may be formed is saponified in the hot alkaline medium. The solution was clarified if necessary, after neutralizing the excess alkali, cooled and acidified. The product usually was dried in ether and purified by vacuum distillation. In preparing higher-melting, less soluble compounds such as the γ -naphthylbutyric acids the toluene layer was separated after allowing the solution to cool to 50–60°, benzene being used if necessary to keep the material in solution and for extraction of the water layer. In case the combined extracts contained coloring matter arising from the presence of impurities in the starting material, it was found most effective to clarify the solution with active carbon while still wet. A part of the solvent was removed by distillation along with any residual water, and on cooling the product

(12) Steinkopf and Wolfram, *Ann.*, **430**, 113 (1923).

(13) Acree, *Ber.*, **31**, 616 (1898).

(14) Borsche and Hallwass, *ibid.*, **55**, 3325 (1922).

crystallized, usually in a very pure condition. To recover the material retained in the mother liquor it was sometimes convenient to steam distil the solvent from a mixture with soda solution, clarify the cooled aqueous solution, and precipitate the product.

In several cases the quantity of the carbonyl compound was increased to 100–150 g. without any essential change in the procedure or in the yield.

Special Cases.—In the reduction of γ -phenylbutyrolactone (Table I), 5 g. of material was used and the mixture was refluxed for thirteen hours. In attempting to reduce β -pyrenoylpropionic acid it was found that both the acid and the ester remained unchanged after long boiling and that the addition of acetic acid led only to the resinification of the product. *o*-Benzoylbenzoic acid was reduced successfully by the modified procedure but the process was less convenient than reduction with zinc dust and alkali and the yield was not as good. Benzyl alcohol was reduced by heating for nine hours a mixture of 25 g. of the material, 50 g. of amalgamated zinc, 90 cc. of concentrated hydrochloric acid and 40 cc. of water, adding 50 cc. more acid from time to time. Fractionation of the mixture yielded 4 g. (19%) of toluene, b. p. 110–113°, and there was considerable high-boiling material. Reduced in the same manner 25 g. of benzyl chloride gave 5 g. (27%) of toluene.

Reduction with Zinc Dust and Alkali

Anthracene from Anthrone.—Twenty-five grams of zinc dust was allowed to stand for a few minutes with an aqueous solution of 0.1 g. of copper sulfate crystals, the solution was poured off and to the activated metal were added 400 cc. of 2 *N* sodium hydroxide, 100 cc. of toluene, and lastly 10 g. of anthrone. The mixture was heated under reflux in an oil-bath and kept boiling gently for twelve hours. The aqueous layer at first assumed a bright red color, after about three hours it turned to a light yellow, and finally both layers became colorless. The mixture was allowed to cool slightly, 100 cc. of benzene was added, and the liquid mixture was transferred to a separatory funnel, using 100 cc. more benzene to wash the zinc residue. The hydrocarbon solution was treated with active carbon while still wet, concentrated to a volume of 50–60 cc., and allowed to cool. The anthracene separated in the form of thin, colorless, highly fluorescent plates, m. p. 216–216.5°, corr.; yield 8.6 g. (93%).

Anthracene from Anthraquinone.—Following the same procedure as above but starting with the quinone it was necessary to continue the refluxing for forty-eight hours and the anthracene, obtained in 80% yield, did not exhibit the beautiful fluorescence of the product from anthrone and melted about one degree lower.

β -Methylanthracene was prepared as above from 2-methylanthrone-9, the yield of once recrystallized material being 86%; m. p. 209–209.5° corr. The yield from β -methylanthraquinone was 80% and the reduction was complete only after four days.

γ -*m*-Methoxyphenylbutyric Acid

β -*m*-Nitrobenzoylpropionic Acid.—To a mechanically stirred mixture of 60 cc. of nitric acid (sp. gr. 1.5) and 6 cc. of concentrated sulfuric acid 30 g. of β -benzoylpropionic acid was added in portions while keeping the mixture at –10 to 0° by efficient cooling. This required twenty to

twenty-five minutes. The temperature was then allowed to rise to 15° in the course of thirty minutes and the solution was slowly stirred into ice and water. The precipitated material was washed free of acid and crystallized from methyl alcohol, giving nearly colorless needles, m. p. 162–164°, corr., of the meta isomer; yield, 21–23 g. (57–62%). The substance crystallizes from water as long, faintly yellow needles.

Anal. Calcd. for $C_{10}H_9O_2N$: C, 53.79; H, 4.07. Found: C, 53.90; H, 4.05.

The methyl ester crystallized from ether-petroleum ether as colorless needles, m. p. 68–69°, corr.

Anal. Calcd. for $C_{11}H_{11}O_2N$: C, 55.67; H, 4.68. Found: C, 55.84; H, 4.63.

β -*m*-Aminobenzoylpropionic Acid.—A solution of 44.6 g. of the nitro compound in 125 cc. of ammonium hydroxide (sp. gr. 0.90) and 75 cc. of water was saturated with hydrogen sulfide, keeping the temperature from rising above 50° by good cooling. The ammonium salt of the starting material at first separated but later redissolved as the exothermic reaction proceeded. The resulting solution was allowed to stand at room temperature for one hour and boiled gently to expel excess gases, the color changing from dark orange-red to yellow-green. The addition of 1–2 g. of sodium hydrosulfite produced a pale yellow solution, and after removing the precipitated sulfur by filtration the solution was boiled with 50 cc. of concentrated hydrochloric acid to coagulate traces of sulfur, it was clarified with active carbon, treated with 50 cc. more of the concentrated acid, and evaporated under vacuum until crystals of the amine hydrochloride began to separate. After thorough cooling the slightly yellow hydrochloride which crystallized was collected and washed with a small amount of cold concentrated hydrochloric acid; yield, 35–40 g. (77–87%). The salt is readily soluble in water and is only partially precipitated by the addition of concentrated hydrochloric acid, giving colorless needles, m. p. above 250° with decomposition.

Anal. Calcd. for $C_{10}H_{12}O_2NCl$: C, 52.27; H, 5.27. Found: C, 52.52; H, 5.30.

The free amine was obtained by adding slightly less than one equivalent of alkali to a solution of the hydrochloride. Thin, colorless plates, m. p. 131–132°, corr., were obtained by crystallization from water (80% conversion).

Anal. Calcd. for $C_{10}H_{11}O_2N$: C, 62.14; H, 5.74. Found: C, 61.95; H, 5.68.

Reduction of the nitro compound with sodium hydrosulfite or stannous chloride was less satisfactory. Dr. E. B. Hershberg employed the method of catalytic hydrogenation with success and obtained about the same yield as above.

β -*m*-Hydroxybenzoylpropionic Acid.—A solution of 7.7 g. of the amine in 35 cc. of water containing 5.5 cc. of concentrated sulfuric acid was cooled to 0° and the paste of the sulfate was treated with a solution of 2.7 g. of sodium nitrite in 10 cc. of water. To the clear solution of the diazonium salt was added 5 cc. of concentrated sulfuric acid and 3.7 g. of boric acid and the mixture was slowly heated to gentle boiling. The evolution of nitrogen was complete soon after the mixture had reached the boiling point. Enough water was added to dissolve the hydroxy com-

TABLE II

Substance	Crystal form	Yield, %	M. p., °C., corr.	Formula	Analyses, %			
					Calcd. C	H	Found C	H
β -3-Nitro-4-methylbenzoylpropionic acid	Needles	78	148-150	$C_{11}H_{11}O_5N$	55.67	4.68	55.75	4.60
Methyl β -3-nitro-4-methylbenzoylpropionate	Needles	90	50-51	$C_{12}H_{13}O_5N$	57.35	5.22	57.49	5.17
β -3-Amino-4-methylbenzoylpropionic acid hydrochloride	Needles	90	144-146	$C_{11}H_{14}O_3NCl \cdot H_2O$	50.46	6.16	50.56	6.12
β -3-Amino-4-methylbenzoylpropionic acid	Fine needles	85	148-149	$C_{11}H_{13}O_3N$	63.74	6.33	63.93	6.22
β -3-Hydroxy-4-methylbenzoylpropionic acid	Plates	80	172-173	$C_{11}H_{12}O_4$	63.43	5.81	63.40	5.83
β -3-Hydroxy-4-methylbenzoylpropionic acid semicarbazone	Needles		188-190	$C_{12}H_{13}O_4N_3$	54.32	5.70	54.13	5.41
β -3-Methoxy-4-methylbenzoylpropionic acid	Fine needles	85	120-121	$C_{12}H_{14}O_4$	64.83	6.35	64.92	6.49
β -3-Methoxy-4-methylbenzoylpropionic acid semicarbazone	Needles		172-173	$C_{13}H_{17}O_4N_3$	55.87	6.14	56.06	5.96
γ -3-Methoxy-4-methylphenylbutyric acid	Thin plates	86	70-71	$C_{12}H_{16}O_3$	69.20	7.75	69.20	7.64

pound and the solution was clarified with charcoal and the slightly yellow filtrate cooled in salt-ice. The product separated as nearly colorless crystals, m. p. 137-140°, yield 7 g. (90%). Crystallization from water (charcoal) gave colorless plates, m. p. 144-145°, corr.; yield 6.2 g. (80%).

Anal. Calcd. for $C_{10}H_{10}O_4$: C, 61.82; H, 5.19. Found: C, 61.63; H, 5.33.

The semicarbazone crystallized from alcohol as colorless needles, m. p. 198-200°, corr.

Anal. Calcd. for $C_{11}H_{13}O_4N_3$: C, 52.57; H, 5.32. Found: C, 52.55; H, 5.46.

β -*m*-Methoxybenzoylpropionic Acid.—A solution of 6.2 g. of the hydroxy compound in 40 cc. of a 10% solution of sodium hydroxide was treated with 6 cc. of dimethyl sulfate at 40-50° and the ester produced was saponified by boiling in alkaline solution. Excess alkali was neutralized and the solution was treated with charcoal. The nearly colorless filtrate was cooled to 40° and acidified, and after thorough cooling the colorless, crystalline product was collected and washed; m. p. 102-104°, yield 6.1 g. (92%). Crystallization from methyl alcohol gave fine, colorless needles, m. p. 107-108°, corr.; yield 5.7 g. (86%). Thompson⁷ reports the melting point of the acid as 110-111°.

Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.43; H, 5.81. Found: C, 63.20; H, 5.76.

The semicarbazone melted at 177-178°, corr., in agreement with the value given by Thompson.

When small amounts (3-5 g.) of the keto acid were reduced by the modified Clemmensen method the toluene layer remained clear and γ -*m*-methoxyphenylbutyric acid of apparently good quality was obtained in the final distillation in 60% yield. With larger amounts (15-25 g.) oily resinous matter separated from the toluene as stated above whether the mixture was boiled from the start or allowed to stand for several hours at room temperature,

and also when the keto acid was added in small portions to the boiling mixture.

γ -3-Methoxy-4-methylphenylbutyric Acid

This acid was prepared from β -*p*-toluylpropionic acid in a series of processes entirely similar to those described above. The yields in the various reactions, given for purified products, and the physical constants and analyses of the compounds are given in Table II.

Summary

1. It is shown that in the reduction of carbonyl compounds by the Clemmensen method improved results are often obtained by adding a layer of toluene to the reaction mixture. The modification is particularly useful in the preparation of γ -arylbutyric acids and in the reduction of compounds containing the methoxyl group. The immiscible solvent also can be used to advantage in the reduction of anthrones to anthracenes with zinc dust and alkali.

2. It is suggested that the Clemmensen reduction of a carbonyl compound proceeds through the alcohol and the chloride, and one or two observations offering some support for this view are recorded.

3. A new route to γ -*m*-methoxyphenylbutyric acid has been investigated and found unsatisfactory in the final step, although by the same process the *m*-methoxy-*p*-methyl derivative can be prepared in good yield.