Rearrangements in the Clemmensen Reduction of 1-Indanones and 1,3-Indandiones[1,2]
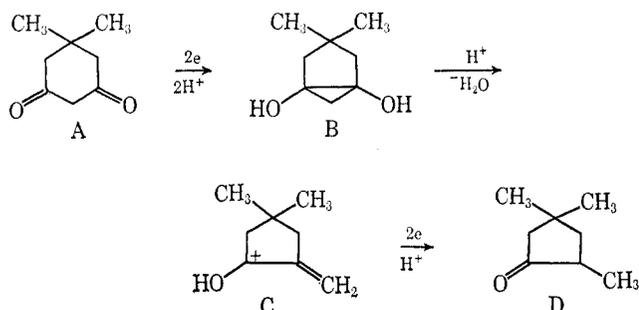
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Clemmensen reduction of 1-indanones and 1,3-indandiones gave both indans and indenes. When the 2 carbon of the starting material held two phenyl groups, the olefinic hydrocarbon product carried a phenyl group at the 1 or 3 position. Saturated indan formation occurred without rearrangement. The monoketones gave largely saturated indans, while 1,3 diketones were reduced primarily to indenes. Both 2,2-diphenyl-1-indanone and 2,2-diphenyl-1,3-indandione gave 2,2-diphenylindan; however, while the monoketone also gave 2,3-diphenylindene, the diketone gave 1,2-diphenylindene. 2,3-Diphenyl-1-indenone on reduction gave cis- and trans-1,2-diphenylindan as major products in addition to some 1,2-diphenylindene. Reduction of both 2-phenyl-1,3-indandione and 2-phenyl-1-indanone gave 2-phenylindan and 2-phenylindene. While cyclopropanediols have been proposed as intermediates in the reduction of 1,3 diketones, such intermediates are not likely in the reduction of 1,3-indandiones, as such bridged compounds would be highly strained. Reaction mechanisms for the formation of the observed products are proposed.

The reduction of aldehydes and ketones to hydrocarbons in the presence of zinc amalgam and concentrated hydrochloric acid is known as the Clemmensen reduction.[4,5] Although mechanisms have been proposed by several investigators,[6-10] they are not yet firmly established. Recently, Davis and coworkers have investigated the Clemmensen reduction of α,β-unsaturated ketones[10] and 1,3 diketones.[7-9] In both systems they found rearranged ketones accompanied by saturated hydrocarbons. In a mechanism proposed by Staschewski[6] for the rearrangement of 5,5-dimethyl-


cyclohexane-1,3-dione (A), the diketone accepts two electrons from zinc metal and two protons to give a diradical. This diradical then couples intramolecularly to form a cyclopropanediol intermediate (B), which, in the presence of acid, rearranges and is further reduced to give 2,4,4-trimethylcyclopentanone (D) as the major product. Davis and coworkers[7-10] presented strong evidence that formation of cyclopropanediol-type intermediates are involved in these reductive rearrangements, since similar compounds also rearrange reductively.[7-10] Olefinic products have not been reported as significant components of these reductive rearrangements.

The present research was undertaken to study the mechanism of the Clemmensen reduction in the 1,3-indandione and 1-indanone systems. Here formation of cyclopropanediol-type intermediates is not favorable because it would require the contraction of an indan derivative to a strained benzbicyclo[2.1.0]pentane system.

Results and Discussion

Reduction of 2,2-Diphenyl-1,3-indandione (2).—2,2-Diphenyl-1,3-indandione was prepared by the phenylation of 2-phenyl-1,3-indandione (1) with di-
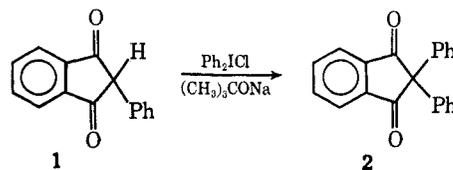
(1) This research was supported by a Petroleum Research Fund type G Grant 1071-G1.
(2) Presented at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Abstract 169.
(3) To whom inquiries should be directed at Columbia University.
(4) E. Clemmensen, Chem. Ber., 46, 1837 (1913).
(5) E. L. Martin, Org. Reactions, 1, 155 (1942).
(6) D. Staschewski, Angew. Chem., 71, 726 (1959).
(7) N. J. Cusack and B. R. Davis, J. Org. Chem., 30, 2062 (1965).
(8) K. M. Baker and B. R. Davis, Chem. Ind. (London), 768 (1966).
(9) B. R. Davis and P. D. Woodgate, J. Chem. Soc., 5943 (1965).
(10) B. R. Davis and P. D. Woodgate, ibid., 2006 (1966).

phenyliodonium chloride in the presence of sodium *t*-butoxide.[11]

Clemmensen reduction of2, 2-diphenyl-1,3-indandione resulted in a mixture of two components as analyzed by vapor phase chromatography (vpc), the previously unreported 2,2-diphenylindan (3) and 1,2-diphenylindene (4), in the ratio of 1:10. Melting point, elemental analysis, ultraviolet spectrum, and nmr spectrum all support 1,2-diphenylindene[12] as the
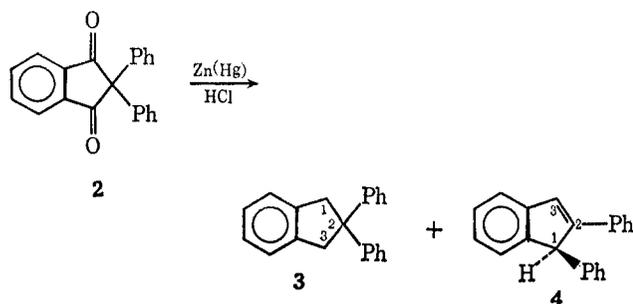

structure of the major product. It was found that 1,2-diphenylindene (4) was isomerized to 2,3-diphenylindene[12] (5) under the conditions of our vapor phase chromatography.
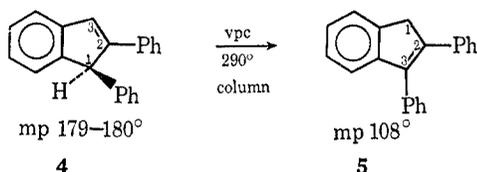
2,2-Diphenylindan (3) was isolated from Clemmensen-reduction mixtures by preparative vapor phase chromatography. Elemental analysis confirmed a $C_{21}H_{18}$ hydrocarbon; ultraviolet data (low ϵ) supported a saturated indan system. The nmr spectrum showed a four-proton singlet at δ 3.51, indicating equivalent C-1 and C-3 protons. On the basis of this data and comparison with the nmr data obtained for the *cis*- and *trans*-1,2-diphenylindans, the structure of 3 was established.

Reduction of 2,2-Diphenyl-1-indanone (6).—When 2,2-diphenyl-1-indanone (6)[13] was reduced under the Clemmensen conditions described, only the saturated 2,2-diphenylindan (3) and the unsaturated rearranged compound 2,3-diphenylindene (5) were obtained, in a ratio of 1.2:1.
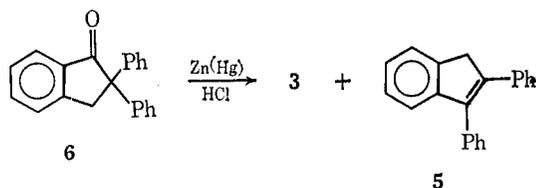
Compound 5 was isolated by vapor phase chromatography and was identified by its infrared spectrum and melting point. Thin layer chromatography of the reaction mixture prior to vpc analysis clearly showed 5 to be the 2,3 olefin. The nmr spectrum of 5 showed a two-proton singlet for the C-1 protons, while the phenyl

(11) F. M. Beringer, S. A. Galton, and S. J. Huang, *J. Amer. Chem. Soc.*, **84**, 2819 (1962).
(12) R. L. Shriner and W. R. Knox, *J. Org. Chem.*, **16**, 1064 (1951).
(13) A. Lüttinghaus and K. Scholtis, *Ann.*, **557**, 70 (1945).

protons gave a 14-proton multiplet centered at δ 7.03 confirming the structure of 5. The uv spectrum of 5 is included in Table I.

TABLE I
ULTRAVIOLET ABSORPTION PEAKS OF SELECTED COMPOUNDS[a]

Compd	λ_{max}, mμ	ϵ_{max}
3	260	1,295
	267	1,540
	273	1,540
4	230[b]	15,500
	305	22,250
	315	21,700
5[c]	235	21,673
	305	20,846
8	261	1,117
	267	1,340
	273	1,020
9	259	1,238
	266	1,453
	273	1,185
11[c]	207	21,930
	262	1,021
	267	1,354
	274	1,321
12	231[d]	14,250
	238	13,950
	246	7,730
	302	25,300
	308	25,500
	315	25,500
14[e]	291	12,900
	302	14,900
	314	21,500
	329	40,500
	345	38,650

[a] Spectra in ethanol, except as noted, were taken on a Cary Model 14 spectrophotometer. [b] Shoulder at 238 and 330 mμ. [c] Spectrum taken in methanol. [d] Shoulder at 300 mμ. [e] Solvent was methylene chloride.

The starting monoketone 6 does not rearrange under the conditions of the Clemmensen reduction in the absence of zinc amalgam.

Reduction of 2,3-Diphenyl-1-indenone (7).—On Clemmensen reduction, 2,3-diphenyl-1-indenone (7) gave three known components, *trans*-1,2-diphenylindene (8),[12,14] *cis*-1,2-diphenylindan (9),[12,14] and 1,2-diphenylindene (4), in a ratio of 1:3:1.
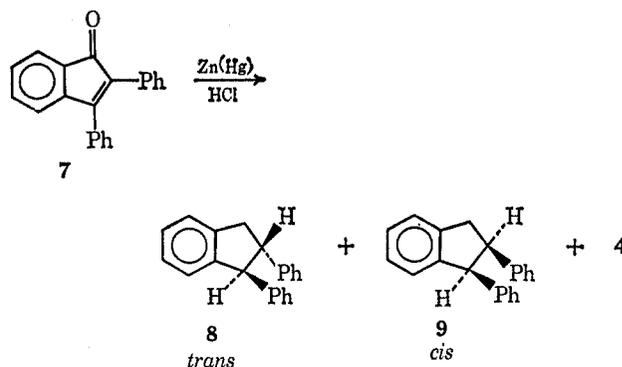
The configurational assignments of 8 and 9 were based on spectra (ir, nmr) identical with those obtained from catalytic hydrogenations of 4 and 5, respectively. As predicted, the 2,3 olefin 5 gave the lower melting

(14) E. Bergman and H. Weiss, *ibid.*, **480**, 64 (1930).

cis-reduction product 9, while the reduction of the 1,2 olefin 4 gave the higher melting, sterically more favorable *trans* isomer 8.

It is of interest to note that Shriner and Knox,[12] in their reduction of compound 7 in ethanol in the presence of zinc amalgam, obtained in addition to compound 4 only *trans*-1,2-diphenylindan (8). We have found that, under there duction conditions reported by these investigators, both *trans*- and *cis*-1,2-diphenylindan were formed in addition to 1,2-diphenylindene. The *cis* isomer was found as the major component, just as in our two-phase reduction system.

**Reduction of 2-Phenyl-1-indanone and 2-Phenyl-1,3-indandione (1 and 10).**—Clemmensen reduction of

1, Z = O
10, Z = H, H

11   12
          1:1.7
          6:1
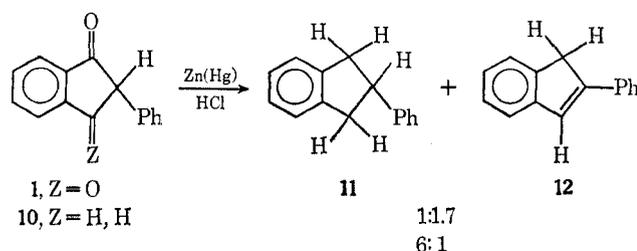
2-phenyl-1-indanone and 2-phenyl-1,3-indandione gave identical saturated and olefinic products, 11 and 12, in relative proportions shown by the equation. The infrared and nmr spectra of the 2-phenylindan[15] (11) and 2-phenylindene[16] (12) from these reductions were superimposable on those obtained for the same products from the Clemmensen reduction of the dehydrodimer of 1 as described below.

Reduction of the Dimer of 2-Phenyl-1,3-indandione (13).—This dimer 13 was obtained as a by-product in the phenylation[11] of 1 and was prepared for this study by dimerization of the anion of 1 with iodine as the oxidizing agent.[17]

1   13
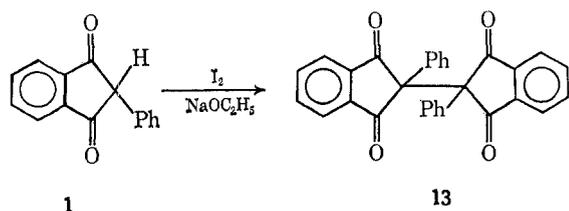
From the Clemmensen reduction of 13, a mixture of hydrocarbons was obtained from which three components were isolated and identified. Vapor phase chromatography of the reaction mixture showed 2-phenylindan (11) and 2-phenylindene (12) in the ratio of 1:1. On cooling the reaction mixture, some of compound 14 crystallized out and was collected as a

13 ⟶ 11 + 12 +
         1:1

14
≥54%
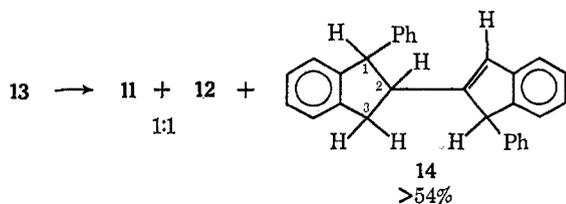
yellow solid. The rest of 14 was eluted with benzene from the chromatography column, giving a total yield of 54% pale yellow needles, mp 277°, mol wt 384 (Rast), and empirical formula $C_{30}H_{24}$. Compound 14 was not eluted from the Apiezon L column under the conditions used for vpc, and therefore its exact concentration in the reduction mixture could not be determined.

Compound 14 was recovered unchanged after attempted catalytic hydrogenation over platinum in ethanol and was not attacked by aqueous potassium permanganate at room temperature. Bromine added to 14 only under forcing conditions. Ozonolysis yielded a carboxylic acid whose structure has not been further investigated.

The ultraviolet spectrum of 14 (Table I) showed high ϵ values, indicating a conjugated unsaturated system. The nmr spectrum of 14 was very similar to that of *trans*-1,2-diphenylindan (8). The assignment of the peaks in 14 was based on relative positions of peaks in 8 and in other compounds listed in Table II. The phenyl protons give rise to a multiplet centered at δ 7.25. Included in this multiplet is the single vinyl proton on C-3, in analogy to the vinyl proton in 2-phenylindene (12). The one-proton doublet ($J_{1,2}$ = 10 Hz) at δ 5.08 is assigned to the C-1 proton *trans* to the C-2 proton. A two-proton multiplet at δ 3.69 represents the proton on C-2 and the proton on C-1. The protons on C-3 give rise to a two-proton doublet ($J_{2,3}$ = 16 Hz) at δ 2.91. Large coupling constants have been reported[18] for various *trans*-1,2-disubstituted indans.

Based on the ultraviolet and nmr data and on the rearrangements found in the Clemmensen reduction of 2,2-disubstituted indandiones, the structure shown is proposed for compound 14. Though not isolated, the *cis* isomer of 14 was probably also formed during the reductive rearrangement. A model of compound 14 in the *trans* form showed the double bond at 2'–3' hindered by the phenyl group on C-1. The relative positions of the groups in this molecule are fixed due to restricted rotation about the 2-2' bond. Lack of reactivity of the double bond may then be explained on steric grounds.

Formation of 2-phenylindan (11) and 2-phenylindene (12) may be accounted for by cleavage of 13 to 1 prior to reduction. Compound 1, as described earlier in this paper, under these conditions is reduced to 11 and 12 in the same ratio as was found in this reduction. Cleavage of 14 after reduction would presumably give rise to 1-phenylindan and 1-phenylindene, which are not found.

Summary and Mechanistic Conclusions.—In the above series of Clemmensen reductions, it was shown that 1-indanones and 1,3-indandiones gave both saturated and unsaturated hydrocarbons. Further, rearrangement of the phenyl group occurred when the 2 position was disubstituted. No ketonic products were found in any of these reductions.

Formation of olefins as major products of usual Clemmensen reduction has not been reported often. However, it was observed by Clemmensen[4] that in dilute hydrochloric acid acetophenone was reduced to styrene rather than to ethylbenzene. More recently,

(15) P. A. Plattner, R. Sandin, and J. Wyss, *Helv. Chim. Acta,* **29,** 1723 (1964).
(16) M. Vaillant, *Ann. Chim.* (Paris), **9,** 5 (1954).
(17) F. M. Beringer, S. A. Galton, and S. J. Huang, *Tetrahedron,* **19,** 809 (1963).

(18) W. E. Rosen, L. Dorfman, and M. P. Linfield, *J. Org. Chem.,* **29,** 1723 (1964).

TABLE II

NUCLEAR MAGNETIC RESONANCE SPECTRA OF SOME INDAN DERIVATIVES[a,b]

Compd	Compd no.	Phenyl protons	C-1	C-2	C-3	Solvent
	3	6.98 (d, 14 H)	3.51 (s, 4 H)	...	3.51 (s, 4 H)	CCl₄
	4	7.10 (m, 15 H)	4.78 (s, 1 H)	...	1 H[c]	CCl₄
	5	7.03 (m, 14 H)	3.74 (s, 2 H)	...	...	CCl₄
trans	8	7.08 (m, 14 H)	4.68[d] (d, 1 H)	3.94 (m, 1 H)	3.32[d] (d, 2 H)	CDCl₃
cis	9	7.08 (m, 14 H)	4.30[d] (d, 1 H)	3.38 (m, 3 H)	3.38 (m, 3 H)	CDCl₃
	11	7.13 (m, 9 H)	3.19[e] (d, 4 H)	3.30 (m, 1 H)	3.19[e] (d, 4 H)	CCl₄
	12	7.19 (m, 10 H)	3.87 (s, 2 H)	...	1 H[c]	CCl₄

[a] Spectra were taken on Varian HR-60 and A-60 spectrometers, using tetramethylsilane (TMS) as internal standard. Chemical shifts are given in parts per million (δ). The letters m, s, and d denote multiplet, singlet, and doublet, respectively. [b] Assignments of the peaks were based on the relative chemical shifts of the protons on the 1, 2, and 3 positions, as described for the 1,2-disubstituted indans [W. E. Rosen, L. Dorfman, and M. P. Linfield, *J. Org. Chem.*, 29, 1723 (1964)]. [c] This proton is included in the phenyl ring multiplet. [d] The coupling constant $J_{1,2} = 8$ Hz. [e] The coupling constant $J_{1,2} = J_{2,3} = 8$ Hz.

Risinger and coworkers[19] found that olefin formation increased with decreasing acid concentration. They ruled out intermediate alcohol formation, as the corresponding alcohols gave much different product ratios: olefins were formed almost exclusively. It has been reported by Vaillant[16] that 2,2-diphenyl-1-indanol during acid-catalyzed dehydration gave only rearranged unsaturated products. The author interpreted these observations as a phenyl migration from the 2 to the 1 position of the intermediate carbonium ion, followed by elimination of a proton. This leaves open the possibility that in reduction of the indanone system rearranged products and olefins may arise from intermediate alcohols.

Still unexplained is the formation of only one isomer, 1,2-diphenylindene, from 2,2-diphenyl-1,3-indandione. Phenyl migration under strongly acidic conditions but without zinc amalgam was shown *not* to occur in the 2,2-diphenylindanones, as these were recovered unchanged from the reaction mixture. Also, olefin formation is *not* an intermediate step in the formation of saturated hydrocarbons, as 1,2-diphenylindene was recovered unchanged when subjected to Clemmensen-reduction conditions.

As mentioned earlier, the present series of compounds was chosen for investigation in part because it was felt that strain would prevent the formation of cyclopropanediol intermediates. In any case, no ring-contracted ketones analogous to D in the introduction were observed.

Proposed Schematic Mechanism.—A mechanism (Schemes I and II) that would account for the above products now follows; the symbol Zn* denotes the zinc metal surface where electron transfers occur.

In the first step the adsorbed ketone is diprotonated on the surface of the zinc (15). Further protonation and loss of water gives an adsorbed cation (16). Loss of zinc ion from 16 with reduction and protonation gives a saturated compound (17). In case of a monoketone the reduction stops here. 1,3 diketones are
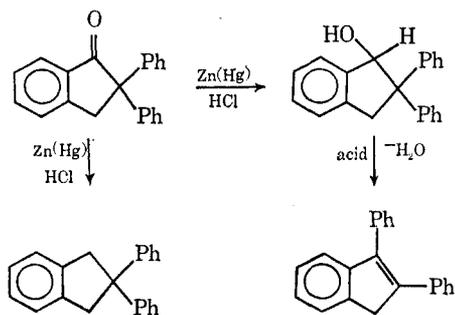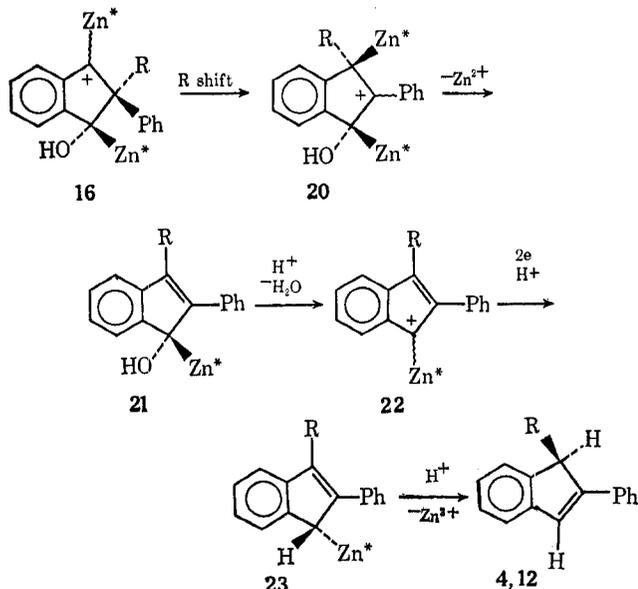
(19) G. E. Risinger, E. E. March, and K. W. Barnett, *Chem. Ind.* (London), 679 (1965).

SCHEME I

MECHANISM FOR REDUCTION TO SATURATED
INDANS WITHOUT REARRANGEMENT

R = H, Ph
Ph = phenyl
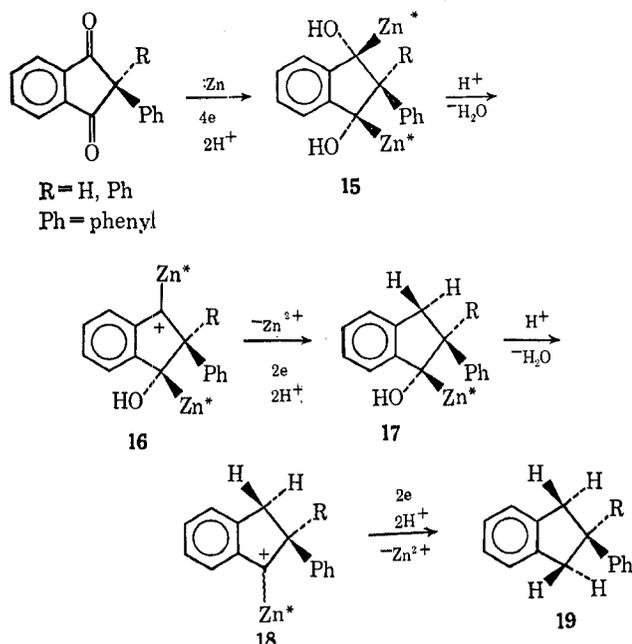
SCHEME II

MECHANISM FOR REDUCTION TO INDENES WITH
REARRANGEMENT

further protonated, followed by loss of water and reduction to give unrearranged saturated hydrocarbons **18** and **19**.

The path for formation of rearranged olefins begins the same way, with formation of cation **16** on the surface of the zinc. Now either saturated indan can be formed without rearrangement or a phenyl group or a hydrogen may shift to form a new cation, **20**. Elimination of zinc from **20** yields a rearranged 2,3 olefin (**21**). In the reduction of the monoketone 2,2-diphenyl-1-indanone the reaction stops here, and the product is compound **5**, 2,3-diphenylindene. 1,3 diketones are reduced further, starting with protonation and elimination of water to form cation **22**. Protonation and

electron release from zinc gives **23**. Finally, the rearranged 1,2 olefin is formed by protolytic cleavage of the bond to the zinc surface.

Experimental Section

General Conditions.—These reductions were run using 5 g of ketone under conditions described by Martin.[5] The amalgamated zinc was prepared from 10 g of granulated zinc and 1 g of mercuric chloride in 15 ml of H₂O and 0.5 ml of concentrated HCl. The liquid was stirred for 5 min and decanted. To the zinc amalgam there was added 7 ml of H₂O, a solution of 5 g of the ketone in 40 ml of toluene, and 17.5 ml of concentrated HCl. This mixture was heated under reflux for 24 hr, during which time three 15-ml portions of concentrated HCl were added. The toluene phase was separated, washed with water, dried, and analyzed for components by thin layer chromatography and vapor phase chromatography on an Apiezon L column at 290°. Separation of components was achieved by preparative vapor phase chromatography and by column chromatography using Florisil as the adsorbent. Purification was achieved by crystallization and distillation. Products were identified by spectral and elemental analyses. Data on individual reductions follow.

Reduction of 2,2-Diphenyl-1,3-indandione (2).—1,2-Diphenylindene (**4**) crystallized from the reaction mixture on cooling; more could be isolated from the organic layer by removal of toluene and trituration with benzene. Recrystallization from ethanol gave white needles of **4**, mp 179–180° (lit.[12] mp 177–178°). Elemental analysis (Table III) supports a C₂₁H₁₆ hydrocarbon;

TABLE III

ELEMENTAL ANALYSES OF THE INDANS AND INDENES[a]

Compd	Formula	Calcd, % C	H	Found, % C	H
3	C₂₁H₁₈	93.29	6.71	93.54	6.92
4	C₂₁H₁₆	93.99	6.01	93.69	6.21
8	C₂₁H₁₈	93.29	6.71	93.16	6.66
9	C₂₁H₁₈	93.29	6.71	93.29	6.68
11	C₁₅H₁₄	92.73	7.27	92.62	7.42
12	C₁₅H₁₂	93.71	6.29	93.48	6.22
14	C₃₀H₂₄	93.71	6.29	93.39	6.34

[a] Analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., and by Galbraith Laboratories, Knoxville, Tenn.

ultraviolet data confirmed the conjugated unsaturated structure by its high ε value. The nmr spectrum is also in accord with the above structure for **4**; deshielding of the C-1 proton in **4** relative to **12** is due to the phenyl ring on that carbon. The vinyl proton at C-3 in both compounds is included in the phenyl-ring multiplet.

2,2-Diphenylindan (**3**) was isolated from a separate reduction by preparative vapor phase chromatography and was purified by distillation at 140° (0.75 mm). The melting point of 2,2-diphenylindan (**3**) was 86–87°. Elemental analysis and spectral data are summarized in Tables I, II, and III.

Reduction of 2,3-Diphenyl-1-indenone (7).—*trans*-1,2-Diphenylindan (**8**), the fastest moving component in this system, was isolated by preparative vpc and by column chromatography (elution with petroleum ether). Its vpc retention time, melting point (126°), and ir spectrum were identical with those of an authentic sample obtained by hydrogenation of 1,2-diphenylindene (**4**) over palladium on charcoal. The uv and analytical data are included in Tables I and III, respectively.

cis-1,2-Diphenylindan (**9**) was isolated as white crystals by preparative vapor phase chromatography and also by column chromatography (elution with 9:1 petroleum ether–benzene). After recrystallization from methanol and two distillations at 150° (0.5 mm), the melting point was 85–86° (lit.[12,14] mp 89°). The ultraviolet spectrum of **9** was very similar to that of the *trans* isomer (Table I). The analytical data are included in Table III.

The nmr spectra of the *cis*- and *trans*-diphenylindans are included in Table I and are also in accord with their proposed structures. In compound **8**, the *trans* isomer, the benzylic proton on C-1 gives a doublet centered at δ 4.68, while in the

cis isomer the same proton appears as a doublet at δ 4.30. The peak for the single proton on the C-2 carbon atom is centered at *ca.* δ 3.94 in compound 8, while in compound 9 this same proton appears at δ 3.38 and is part of the three-proton multiplet that includes the two protons on C-3. This additional shielding of the C-1 and C-2 protons in 9 is probably due to the *cis* configuration of these protons. It appears that the chemical shift of the protons on the C-3 position is not effected by the stereochemistry at C-1 and C-2.

The olefinic compound, the slowest moving component, had a retention time on vpc identical with that of 1,2-diphenylindene (4). Compound 4 as indicated before, isomerizes to the 2,3 isomer under these vpc conditions and therefore could not be isolated by preparative vpc. In addition, compounds 8 and 9 could not be separated from compound 4 by column chromatography on Florisil. The structure of this compound had to be established by an alternative method as follows: an authentic sample of 1,2-diphenylindene (4) was isomerized to the 2,3 isomer (5) by a known procedure[12] in the presence of hot alcoholic potassium hydroxide. The melting point (108°) of the pale yellow crystals obtained on recrystallization from ethanol corresponds with that reported for this compound (5).

Thin layer chromatography on silica gel with 99:1 petroleum ether-benzene as the eluent gave an excellent separation of the two isomeric diphenylindenes; the 2,3 isomer (5) moved much faster than the 1,2 isomer (4). We were thus able to establish that in the above reaction mixture the olefin formed was indeed 1,2-diphenylindene (4).

Catalytic Hydrogenation of 1,2-Diphenylindene (4).—A solution of 200 mg of 4 in 50 ml of ethanol was hydrogenated in the presence of 250 mg (0.93 mmol) of 5% palladium on charcoal at 50 psi. After 30 min the catalyst was removed, and the filtrate was concentrated to 15 ml and allowed to crystallize. The fine white needles were collected to yield 150 mg (0.56 mmol, 60%) of *trans*-1,2-diphenylindan (8), mp 119–121°. Sublimation at 100–110° (0.1 mm) raised the melting point to 125–126° (lit.[12] mp 126°).

Catalytic Hydrogenation of 2,3-Diphenylindene (5).—To 100 mg of 10% palladium on charcoal there was added a solution of 1

g of 5 in 150 ml of benzene. This mixture was hydrogenated under 30 psi for 5 hr. After filtration through Celite and evaporation of the solvent, there was found by vpc analysis *cis*-1,2-diphenylindene (9) and unchanged 5 in the ratio of 1:2.2. Compound 9 and 5 were separated by preparative vpc and their identities were confirmed by their ir spectrum.

Reduction of 2-Phenyl-1-indanone and 2-Phenyl-1,3-indandione (10,1).—Separation of 2-phenylindan (11) and 2-phenylindene (12) was achieved by column chromatography. From the petroleum ether fraction, 11 was obtained as a colorless oil, which was distilled *in vacuo* at 100–110° (0.1 mm). The reported[15] boiling point for this compound is 165° (11 mm).

The second component, 2-phenylindene (12), was present in the 9:1 petroleum ether–benzene eluate. Shiny white flakes were collected on evaporation of the solvent. On recrystallization from hexane these melted at 167–168° (lit.[16] mp 167.5°). Correct analysis was obtained for a $C_{15}H_{12}$ hydrocarbon, and the ultraviolet spectrum (high ε) confirms that this is a conjugated unsaturated compound. The nmr spectra of 11 and 12 are included in Table II.

Reduction of the Dimer of 2-Phenyl-1,3-indandione (13).—Separation of 2-phenylindan (11) and 2-phenylindene (12) from the reaction mixture was achieved by column chromatography as in the previous reduction. Identity of these compounds with 11 and 12 obtained from the reduction of 1 was established by boiling points, mixture melting points, and infrared spectra. Isolation, characterization, and proposed structure of 14 are described in detail earlier in the paper.

Circular Dichroism of Monocyclic and Bicyclic Lactones. Restricted and Rigid Model Compounds for the Ester Chromophore

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The optical properties of monocyclic dilactones and of bicyclic bridged lactones have been examined using circular dichroism. In the 210–220-mμ region, the sign of the Cotton effect for the monocyclic dilactones (*S,S*)-3,6-dimethyl-1,4-dioxane-2,5-dione (I) and (*R,R*)-3,6-diphenyl-1,4-dioxane-2,5-dione (II) is opposite that of acyclic model compounds. Two new dichroic bands at 210 and 199 mμ have been observed in the circular dichroism spectra of 1,8,8-trimethyl-3-oxabicyclo[3.2.1]octan-2-one (III). Solvent and conformational effects on the dichroic properties of this bridged lactone (III) are assignable, because the molecule is essentially conformationally rigid.

Ultraviolet (uv),[1] optical rotatory dispersion (ORD),[2] and circular dichroism (CD)[3] studies of saturated lactones have recently attracted considerable attention.

The relationship between conformation and absolute configuration of these compounds and sign and magnitude of long-wavelength Cotton effects has been studied extensively. Four different approaches to this problem have been made independently by Klyne,[4] Snatzke,[5] Wolf,[6] and Legrand.[7]

The growing interest in the stereochemistry of optically active polyesters[8] prompted us to examine the rotatory properties of mono- and bicyclic lactones, since we believed that the transitions involved in the

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