Sigmatropic Indenyl Rearrangements Induced by Electron Transfer Reduction

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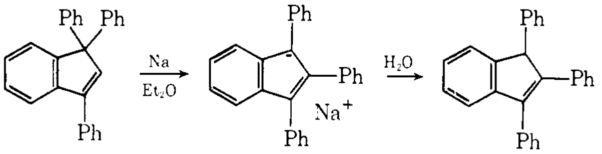
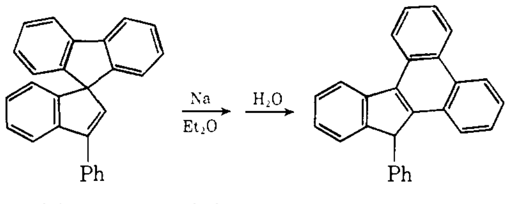
Received February 13, 1970

Abstract: Several 1,1-disubstituted indenes were reduced with alkali metals in tetrahydrofuran (THF) and ether solvents. Using sodium–potassium in THF followed by quenching with water, the following reactions were observed: 1,1,3-triphenylindene produced 1,2,3-triphenylindan; 1,1-diphenylindene produced 1-phenylindene and 2,3-diphenylindene; and 1-methyl-1-phenylindene led to 3-methyl-2-phenylindene. In each case products arise from phenyl migration in an intermediate radical anion or dianion. In contrast to phenyl, methyl does not migrate. 1,1-Dimethylindene reduction with sodium–potassium in THF followed by quenching with water gave 1,1,1′,1′-tetramethyl-2,2′-diindan.

Molecular rearrangements are of inordinate interest to chemists. The sigmatropic reorganization of neutral molecules, cations, anions, radicals, and carbenes have all received considerable attention. The study reported here explores the possibility of sigmatropic radical anion rearrangements. Such reactions have not been investigated and the facility of reorganization cannot be readily predicted from other work. It is important to realize that radical ions are species distinct from either radicals or ions so that their chemistry cannot be confidently prejudged from examples involving the classical intermediates of organic chemistry: carbonium ions, carbanions, or free radicals. The present paper is based on the reductive rearrangement of 1,1,3-triphenylindene which was discovered, but misinterpreted by Schlenk and Bergmann.[1] The following reinterpretation was suggested by Ziegler and Crossman[2] and a closely related example was later discovered by Koelsch.[3]





In addition to providing a system to test the facility of reductive sigmatropic rearrangements, such reactions are of interest for comparison with thermal[4] and photochemical[5] indene substituent migrations.

Experimental Section

All nmr spectra were recorded with a Varian A-60A spectrometer and chemical shifts are reported in τ units. Infrared spectra of solid samples were obtained from KBr pellets, and liquids were run as smears between salt plates. Measurements were made on either a Perkin-Elmer Model 457 grating spectrometer or a Unicam Model SP-1200. All infrared data are presented in microns using a polystyrene film for a standard. Gas chromatographic analysis was carried out on an F&M Research Chromatograph Model 5750, equipped with a programmed temperature unit and thermal conductivity cell. The column used was an F&M 6-ft, 10% UC-W98 80-100-S. Mass spectral data were measured with an AEI Model MS-12 spectrometer. For exact mass measurement, heptacosafluorotributylamine was used. The data are presented by reporting *m/e* (per cent of base peak). Galbraith Laboratories, Inc., of Knoxville, Tenn. performed elemental analyses. Melting points were measured with a Fisher-Johns apparatus and are uncorrected.

The preparation of 1,1,3-triphenylindene, 1,1-diphenylindene, 1-methyl-1-phenylindene, 2,3-diphenylindene, and 3-methyl-2-phenylindene have been described.[4]

3,3-Dimethyl-1-indanone. This compound was prepared following the procedure of Bosch and Brown.[6] Vacuum distillation provided a fraction of light, clear, oil: bp 78–85° (0.70 mm) (lit.[6] 80°); yield 10.7 g (67%). The nmr spectrum (CCl_4) displayed a singlet at 8.6 (6 H), a singlet at 7.5 (2 H), and a complex multiplet centered at 2.5 (4 H).

3,3-Dimethyl-1-indanol. $LiAlH_4$ reduction of 3,3-dimethyl-1-indanone produced a colorless, viscous oil, bp 85–90° (0.70 mm) (lit.[6] 87°). The nmr spectrum (CCl_4) gave singlets at 8.88 (3 H) and 8.71 (3 H), a multiplet centered at 8.1 (2 H), a broad singlet at 5.83 (1 H), a triplet at 4.95 (1 H), and a singlet at 2.85 (4 H).[6]

1,1-Dimethylindene. A 67% yield of this olefin was prepared by dehydrating 3,3-dimethyl-1-indanol (8.0 g) with *p*-toluenesulfonic acid in acetic acid (1.6 g in 50 ml). After a reflux time of 1 hr the reaction mixture was poured into 100 ml of ice water. Ether extraction provided an oil which was purified by vacuum distillation: bp 63–65 (7.6 mm) (lit.[6] 52° at 4.8 mm); nmr spectrum singlet at 8.73 (6 H), AB quartet at 3.58 (2 H), and a multiplet at 2.8 (4 H).[6]

1,1-Diphenylindene. The procedure of Brown and Jackman[7] was used to dehydrate 3,3-diphenyl-1-indanol.[4] The alcohol was dissolved in a solution of *p*-toluenesulfonic acid in acetic acid. After work-up and crystallization of the product from 95% ethanol, clear crystals (45%) were obtained, mp 91–92° (lit.[7] 91–92°). The nmr spectrum ($CDCl_3$) displayed singlets at 3.2 (2 H) and 2.75 (14 H).

2,2-Dideuterio-3,3-diphenyl-1-indanone. Lithium metal (0.06 g, 0.086 g-atom) was added to 2 ml of D_2O. 3,3-Diphenylindanone[4] (0.5 g, 0.0018 mol) was dissolved in 5 ml of dry tetrahydrofuran (THF). Both solutions were warmed to 70°. They were poured together and refluxed for 3 hr. The reaction mixture was neutralized with 10% DCl and extracted with anhydrous ether. The ether layer was dried ($MgSO_4$) and concentrated on a rotary evaporator leaving a white solid (0.5 g. 100%), mp 132–133°. The nmr spectrum ($CDCl_3$) showed absorptions at 2.8.

2,2-Dideuterio-3,3-diphenyl-1-indanol. To 0.5 g of 2,2-dideuterio-3,3-diphenyl-1-indanone dissolved in 5 ml of dry ether was added

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(1) W. Schlenk and E. Bergmann, *Justus Liebigs Ann. Chem.*, 463, 125 (1928).

(2) K. Ziegler and F. Crossman, *Ber. Deut. Chem. Ges. B*, 62, 1768 (1929).

(3) C. F. Koelsch, *J. Amer. Chem. Soc.*, 56, 480, 1605 (1934).

(4) L. L. Miller and R. F. Boyer, *ibid.*, 93, 650 (1971).

(5) J. J. McCullough, *Can. J. Chem.*, 46, 43 (1968).

(6) A. Bosch and R. K. Brown, *ibid.*, 42, 1718 (1964).

(7) R. F. Brown and L. M. Jackman, *J. Chem. Soc.*, 3144 (1960).

a solution of 0.33 g of $LiAlH_4$ in 5 ml of dry ether. The solution was heated to reflux for 3 hr. Dropwise addition of water-saturated ether was used to quench the reaction. The aluminum and lithium hydroxides were filtered from the ether and washed with several small portions of ether. The combined ether fractions were dried ($MgSO_4$) and concentrated on the rotary evaporator, leaving fine white needles (0.4 g, 78%), mp 138–138.5°. Absorptions in the nmr spectrum ($CDCl_3$) included a broad singlet at 8.14 (1 H), a singlet at 4.82 (1 H), and a singlet at 2.78 (14 H).

2-Deuterio-1,1-diphenylindene. 2,2-Dideuterio-3,3-diphenyl-1-indanol (0.4 g) dissolved in 20 ml of glacial acetic acid was treated with 0.05 g of *p*-toluenesulfonic acid. The reaction mixture was heated to reflux for 1 hr and poured into 50 ml of water. The water solution was extracted with ether which was washed with 10% sodium carbonate until all acetic acid was removed. After drying ($MgSO_4$) and concentration of the ether solution, a white solid was obtained (0.2 g, 72%). After crystallization from 95% ethanol, clear crystals, mp 90° were obtained. Two sharp singlets at 3.2 (1 H) and 2.75 (14 H) were displayed in the nmr spectrum ($CDCl_3$). The prominent peaks in the mass spectrum were: 269 (100%), 268 (40%), 266 (17%), 192 (17%), 190 (13.5%), and 126.5 (17%).

1-Deuterio-3,3-diphenylindanol. Into a 50-ml flask is placed 0.50 g of 3,3-diphenylindanone dissolved in 20 ml of dry ether and 0.07 g of $LiAlD_4$ dissolved in 5 ml of dry ether. After refluxing for 3 hr, the reaction was worked up as in the preparation of 3,3-diphenyl-1-indanol. The white solid remaining (0.3 g, 60%) was recrystallized from benzene–Skellysolve H (1–2) and had a mp of 138°. The nmr spectrum ($CDCl_3$) consisted of a singlet at 8.14 (1 H), double doublets centered at 7.0 (2 H), and a singlet at 2.78 (14 H).

3-Deuterio-1,1-diphenylindene. 1-Deuterio-3,3-diphenylindanol (0.3 g) was dissolved in 10 ml of acetic acid and treated with 0.04 g of *p*-toluenesulfonic acid. After refluxing for 1.5 hr, the reaction mixture was worked up as described for the preparation of 2-deuterio-1,1-diphenylindene. A white solid (0.15 g, 53%), mp 90°, was obtained after recrystallization from 95% ethanol. The nmr spectrum ($CDCl_3$) was identical with that obtained for 2-deuterio-1,1-diphenylindene. The prominent peaks in the mass spectrum were: 269 (100%), 268 (48%), 266 (23%), 253 (14%), 192 (17%), 190 (14%), and 126.5 (12%).

2-Deuterio-1,1,3-triphenylindene. Phenylmagnesium bromide was prepared from 0.5 g of bromobenzene and 0.07 g of magnesium ribbons in 10 ml of dry THF. 2,2-Dideuterio-3,3-diphenyl-1-indanone was dissolved in 10 ml of dry THF and added dropwise to the Grignard reagent. After warming to reflux for 1 hr, 10% H_2SO_4 was added. Again the product contained deuterated alcohol and olefin. If this product mixture was heated with 10 ml of acetic acid and 0.1 g of *p*-toluenesulfonic acid, 0.3 g of the desired hydrocarbon was obtained, mp 136°. Prominent mass spectral peaks included: 345 (100%), 268 (60%), 266 (95%), 240 (25%), 190 (17%), and 77 (7%). The nmr spectrum displayed a peak at 2.78.

1,2,3-Triphenylindan. 1,2,3-Triphenylindene (0.5 g) was dissolved in 25 ml of *n*-amyl alcohol. Small pieces of freshly cut sodium metal (1 g) were added to the refluxing alcohol solution. After a reflux time of 2 hr, the sodium disappeared. The reaction mixture was worked up by quenching with 5 ml of water and then extracting with ether. After drying ($MgSO_4$), and removing the ether and alcohol by distillation, a white crystalline solid was obtained. Upon further purification on a silica gel column, eluting with 20% benzene–80% Skellysolve H, 0.3 g of a white solid was obtained, mp 146–147° (lit.[8] 154°). Peaks in the nmr spectrum (CCl_4) included a triplet at 5.9 (1 H) (J = 7 cps), doublet at 5.1 (2 H) (J = 7 cps), multiplet at 3.2–3.6 (5 H), a singlet at 2.96 (10 H), and another singlet at 2.7 (4 H). The uv spectrum gave λ_{max} 227 (ϵ 7000) and λ_{max} 268 nm (ϵ 800). The mass spectrum had peaks at 346 (26%), 269 (61%), 256 (52%), 178 (65%), 165 (83%), 91 (61%), and 78 (100%).

Anal. Calcd for $C_{27}H_{22}$: C, 93.6; H, 6.36. Found: C, 93.75; H, 6.26.

Alkali Metal Reduction of Substituted Indenes. Tetrahydrofuran (THF) and 1,2-dimethoxyethane (glyme) were dried by distilling from $LiAlH_4$ under an atmosphere of nitrogen. Anhydrous ether was used as obtained from Matheson Coleman and Bell or distilled from $LiAlH_4$. Hexamethylphosphoramide was obtained from Aldrich Chemical and was not further purified. Sodium–potassium alloy was prepared by melting together, under xylene, five parts of freshly cut potassium and two parts of sodium metal. It is liquid above −10°.

In one neck of a 50- or 100-ml three-necked, round-bottomed flask was placed a condenser with a gas outlet leading to a mercury bubbler. A gas inlet tube (N_2) was in another opening while the third neck was used to distill the solvent into the reaction flask. A glass-covered magnetic stir bar was necessary because the alloy was quite corrosive to Teflon stirring bars. The compound to be reduced was dried thoroughly, either in a vacuum oven or by the use of an abderhalden with P_2O_5 as the drying agent, and weighed into the reaction flask (0.5–1.0 g). The desired solvent was then distilled into the reaction vessel. While flushing with prepurified, dry nitrogen, 3–6 drops of the alloy were added to the hydrocarbon dissolved in the solvent. At the desired time, the reaction was quenched and the excess alloy decomposed by the dropwise addition of water-saturated ether. The work-up procedure included drying the ether–THF solution ($MgSO_4$), and concentrating under vacuum. The products were isolated and purified by gas chromatography, column chromatography, or recrystallization.

1,1,3-Triphenylindene Reduction. A. Following the procedure outlined in the reduction method section, 0.5 g of 1,1,3-triphenylindene in dry ether was treated with 0.1 g (4 equiv) of freshly cut sodium metal. A blue-violet color immediately began to stream from the metal surface, which soon spread to the whole solution. After 10 hr, work-up gave a white crystalline solid, mp 135° (95% ethanol), which upon comparison with known 1,2,3-triphenylindene was found to be identical; yield, 0.45 g (90%).

B. Procedure A was repeated except THF was exchanged for ether. A deep red color formed when the sodium metal was added to the THF solution of the hydrocarbon. After 10 hr, work-up produced 0.4 g (80%) of a white solid, mp 147°. The solid, after recrystallization from 95% ethanol, was found to be identical in all respects with authentic 1,2,3-triphenylindan.

C. The outlined procedure was carried out with 0.5 g of the indene, 100 mg of Na–K alloy, and 25 ml of THF. A dark red-purple color appeared. After a 12-hr reduction period and typical work-up, a white solid was obtained (mp 143–145°), which was further purified on a silica gel column, eluting with Skellysolve H. Collecting 200 ml in each fraction, crystals were found in fractions 11–15 (0.40 g, 80%), mp 147°. The product agreed in all respects with the product from procedure B, 1,2,3-triphenylindan. When this reduction with Na–K was repeated and quenched by the addition of 5% DCl instead of wet ether, a white solid was again obtained, mp 146–147° (95% ethanol). The nmr spectrum showed a singlet at 5.88 (1 H), a multiplet at 3.2–3.6 (5 H), a singlet at 2.96 (10 H), and another singlet at 2.7 (4 H). Mass spectral measurement gave a parent peak of *m/e* 348. The product was shown to be 1,3-dideuterio-1,2,3-triphenylindan.

2-Deuterio-1,1,3-triphenylindene Reduction. Following the general procedure of reduction with 0.31 g of this compound, 50 mg of Na–K alloy, and 25 ml of dry THF provided 0.3 g (96%) of a white crystalline solid, mp 146–147°. The nmr spectrum showed a singlet at 5.08 (2 H), a multiplet at 3.2–3.6 (5 H), a singlet at 2.96 (10 H), and a singlet at 2.7 (4 H). The product, 2-deuterio-1,2,3-triphenylindan, gave a parent ion of *m/e* 347.

1,1-Diphenylindene Reduction. A. An attempt to reduce this olefin with sodium metal in dry ether proved fruitless, as no color could be detected and starting material was recovered after 24 hr.

B. When the reduction was carried out in dry THF with Na–K alloy, the reaction mixture immediately became red-brown. The general work-up procedure yielded a yellow oil. Gas chromatographic analysis detected two components. The oil was eluted on an alumina column using Skellysolve as eluent. Collecting 250-ml fractions, fraction 5 contained an oil (35%) and fractions 8–11 contained a light yellow solid (65%). The oil in fraction 5 gave an nmr spectrum consisting of a doublet at 6.6 (2 H) (J = 2 cps), triplet at 3.50 (1 H) (J = 2 cps), and a multiplet centered at 2.6 (9 H). The uv spectrum had three peaks: λ_{max} 207 (ϵ 25,000), λ_{max} 230 (ϵ 20,000), and λ_{max} 260 nm (ϵ 10,000). The mass spectrum gave a parent peak at *m/e* 191. Unequivocal synthesis and published nmr[9] and uv spectra[10] indicate that this product is 3-phenylindene. The crystals in fractions 8–11 could be recrystallized from 95% ethanol, mp 110°, and had for the uv spectrum λ_{max} 237 (ϵ 20,000) and 307 nm (ϵ 18,000). It showed nmr peaks ($CDCl_3$) at 6.12, singlet (2 H), and 2.75–2.63 (14 H). This compound, 2,3-diphenylindene, agreed in all respects with those properties published by McCullough.[5]

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(8) E. P. Kohler and W. E. Mydans, *J. Amer. Chem. Soc.*, **54**, 4667 (1932).

(9) A. S. Kende and T. L. Bogard, *Tetrahedron Lett.*, 3383 (1967).

(10) K. Bott, *ibid.*, 4569 (1965).

Table I. Reaction Products[a]

Reactant	Solvent	Metal	Product (% yield)[b]
1,1,3-Triphenylindene	Ether	Na	1,2,3-Triphenylindene (90)
	THF	Na	1,2,3-Triphenylindan (90)
	THF	Na, K	1,2,3-Triphenylindan (80)
	Amyl alcohol	Na	1,1,3-Triphenylindan
1,1-Diphenylindene	THF[c]	Na, K	2,3-Diphenylindene (65) 3-Phenylindene (35)
1-Methyl-1-phenylindene	THF	Na, K	3-Methyl-2-phenylindene (65)
1,1-Dimethylindene	THF	Na, K	1,1,1′,1′-Tetramethyl-2,2′-diandan (90)

[a] Products isolated after quenching the reaction with wet ether. [b] Based on purified product compared to initial amount of reactant. [c] Dimethoxyethane and hexamethylphosphoramide gave very similar product yields.

1-Methyl-1-phenylindene Reduction. Following the general procedure, 0.50 g of the indene was dissolved in 50 ml of freshly distilled THF. Sodium–potassium alloy (150 mg) was added and the solution turned green, finally dark purple. After 10 hr, the reaction was quenched by the addition of wet ether. Work-up gave 0.45 g of an oil which when subjected to gas chromatography showed the presence of two compounds. By comparing the retention time for known starting material, one component was shown to be 1-methyl-1-phenylindene. The second component could be isolated by dissolving the mixture in a minimum amount of petroleum ether (bp 35–40°). Light yellow crystals separated after cooling, mp 80°; yield, 66%. Peaks obtained in the nmr spectrum were: triplet at 7.75 (3 H) (J = 2 cps), quartet at 6.35 (2 H) (J = 2 cps), and a multiplet at 2.5–3.0 (9 H). The mass spectrum recorded a parent ion of m/e 206. An alternate synthesis gave evidence for 2-phenyl-3-methylindene as the product.[11,12]

1,1-Dimethylindene Reduction. This hydrocarbon was easily reduced by the action of Na–K in dry THF. When the reactants were mixed (1 g of olefin, 6 drops of alloy, and 50 ml of THF), a bright red color developed. After 10 hr and a typical work-up, a light oil was obtained. This oil was chromatographed on alumina, using Skellysolve H-benzene (90:10) as eluent. Collecting 100-ml fractions, crystals were obtained in fractions 15–18. These crystals, mp 122–122.5° (ethanol), gave a parent ion in the mass spectrum of m/e 290. Other prominent peaks were: 48 (100%), 49 (85%), 84 (65%), 116 (15%), 131 (18%), and 145 (5%). The nmr recorded peaks at 8.98 (3 H), 8.68 (3 H), four peaks centered at 7.78 (1 H), three peaks centered at 7.1 (2 H), and a singlet at 2.9 (4 H). The ir spectrum (KBr) for this product, 1,1,1′,1′-tetramethyl-2,2′-diindan, gave a doublet at 7.28–7.38.

Anal. Calcd for $C_{22}H_{26}$: C, 91.03; H, 8.97. Found: C, 91.02; H, 9.07.

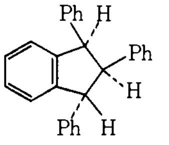
1,1-Diphenylindene Reduction in Glyme. Dimethoxyethane was distilled from $LiAlH_4$ into a reaction vessel as previously described. When 150 mg of Na-K alloy was added, a red-brown color developed. After 11 hr of reduction, a typical work-up provided 0.8 g of an oil, which upon separation on an alumina column gave 3-phenylindene (33%), and 2,3-diphenylindene (65%).

1,1-Diphenylindene Reduction in Hexamethylphosphoramide. Following the normal procedure, the reaction mixture turned dark blue after the addition of the alloy (125 mg). After 24 hr, the reduction was quenched with wet ether. Gas chromatographic analysis showed the presence of 3-phenylindene and 2,3-diphenylindene in a ratio of about 3:6.

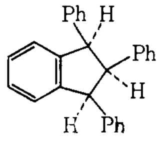
Results and Discussion

Several substituted indenes were prepared using methods previously reported. Only one anomaly was noted. The nmr spectrum of the supposed 1,1-diphenylindene showed singlets at τ 3.2 (2 H) and 2.75 (14 H). It was suspected that the 3.2 peak resulted from the accidental degeneracy of the hydrogens at C-2 and C-3. This was confirmed by synthesizing 2-deuterio- and 3-deuterio-1,1-diphenylindene. These compounds have identical spectra with singlets at τ 3.2 (1 H) and 2.75 (14 H).

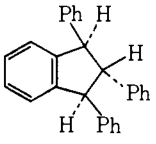
The substituted indenes were treated with either excess sodium or sodium–potassium alloy in ethereal solvents. The products of these reactions are summarized in Table I. Analysis by nmr of the crude reaction mixtures or work-up and isolation gave consistent results in each case. The products were characterized spectrally and by comparison with known samples. Although 1,2,3-triphenylindan had not been spectroscopically characterized, its spectra are in agreement with this structure. The equivalence of the protons on carbons 1 and 3 indicates that the structure cannot be cis,trans. A decision between cis,cis and the more stable trans,trans cannot be made with complete confidence. The two 1,2-diphenylindene stereoisomers have been characterized.[13,14] *cis*-1,2-Diphenylindan has the C-1 proton at τ 5.70, the C-2 proton at 6.62 ($J_{1,2}$ = 8 cps). *trans*-1,2-Diphenylindene has the C-1 proton at 5.32 and the C-2 proton at 6.06 ($J_{1,2}$ = 8 cps). Both protons are at lower field when cis to a phenyl. Triphenylindan absorbs at: C-1, 5.1; C-2, 5.9. This compares well with *trans*-diphenylindan and the assignment *trans,trans*-triphenylindan is tentatively made.



cis–trans



cis–cis



trans–trans

A number of atypical reduction products have been discovered in this work. In fact, one of the few "normal" products is the reduced dimer from 1,1-dimethylindene reduction. The structure 1,1,1′,1′-tetramethyl-2,2′-diindan is established by the spectra and microanalysis. The stereochemistry is unknown. Reductive dimerization is well known and appears to arise from radical anion dimerization.[15–17] A close analog is found in the dimerization of α-methylstyrene and diphenylethylene radical anions.[18] The latter has been studied

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(11) H. Christol, C. Martin, and M. Mousseron, *Bull. Soc. Chim. Fr.*, 1696 (1960).

(12) N. D. Heindel, S. M. Lemke, and W. A. Mosher, *J. Org. Chem.*, **31**, 2680 (1966).

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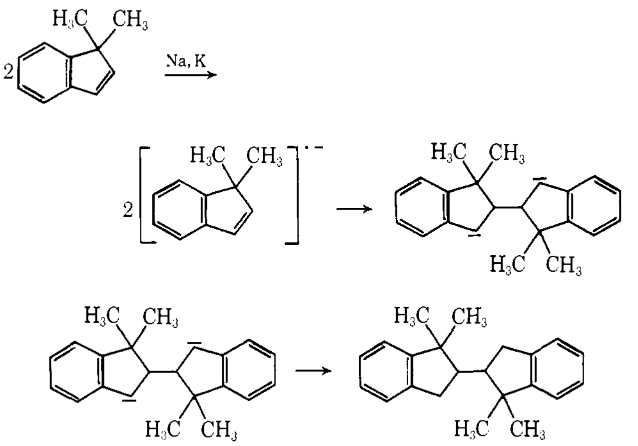
(14) S. A. Galton, M. Kalafer, and F. M. Beringer, *ibid.*, **35**, 1 (1970).

(15) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, pp 50–77.

(16) W. Schlenk, *et al.*, *Chem. Ber.*, 47, 473 (1914).

(17) J. B. Conant and A. H. Blatt, *J. Amer. Chem. Soc.*, **50**, 551 (1928).

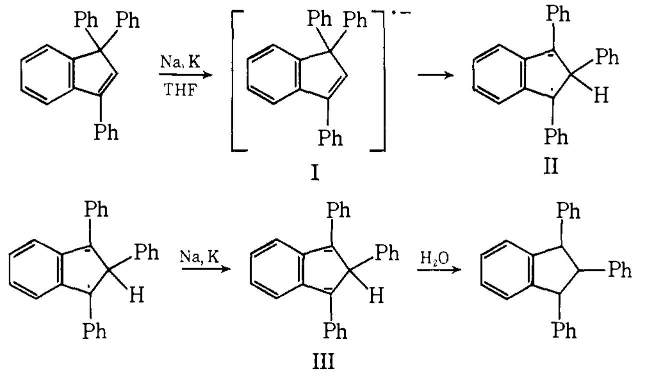
(18) J. L. R. Williams, T. M. Laasko, and W. J. Dalmage, *J. Org. Chem.*, **23**, 638 (1958).



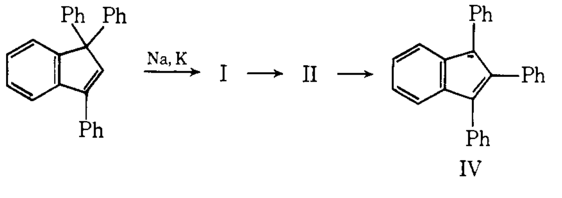
in detail by Szwarc and coworkers[19] who measured a second-order rate constant of 3×10^6 l. sec^{-1} mol^{-1} at 26° in THF.[20]

All other reactants in the present study were 1-phenyl derivatives and in each case rearrangement precludes dimerization. 1-Methyl-1-phenylindene, for example, produces no dimer even though the rate constant for radical anion dimerization should be very similar to that for 1,1-dimethylindene radical anions. Although phenyl migrates much faster than methyl, both reactions are slower than protonation. Reduction of 1,1,3-triphenylindene in alcohol gives 1,1,3-triphenylindan.

In attempting to bring some order to the remaining data, triphenylindene in tetrahydrofuran (THF) will be arbitrarily chosen as a reference system. In THF, reduction proceeds approximately as follows. Initial reaction is electron transfer into a diphenylethylene π electrophore.[21] This can be followed by rearrangement to form a more stable *o*-quinodimethane type anion radical (II) which is also stabilized by an additional phenyl group compared to I. Further reduction then leads to a dianion product, III, which is protonated on quenching. Alternatively, the second electron transfer could precede rearrangement since an unstable dianion corresponding to I might be very reactive.



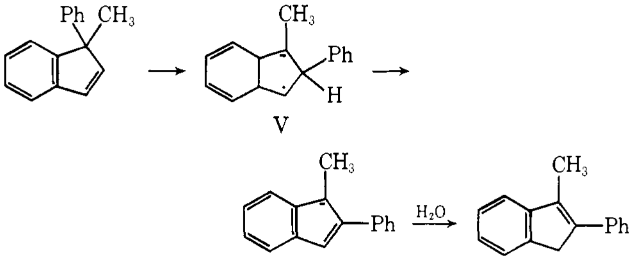
Eventual formation of dianion III is indicated by the absence of indene products which should result from a monoanion (II).[22] Confirmation of this scheme is offered by two studies using isotopic labeling. (1) The reduction of 1,1,3-triphenylindene followed by quenching with deuterium oxide produced exclusively 1,3-dideuterio-1,3-triphenylindan. (2) Reduction of 2-deuterio-1,1,3-triphenylindene with sodium in THF produced 2-deuterio-1,2,3-triphenylindan. This rules out a process involving overreduction of an initially formed indenyl anion (IV), an *a priori* feasible process since IV is formed in ether and THF could promote addition of a second electron. Similar reductions of anions to dianion radicals have been reported for the 9-phenylfluorenyl anion[23] and the cycloheptatrienyl anion.[24]



(1)

1,1,3-Triphenylindene reduced in ether and quenched with water gives 1,2,3-triphenylindene. This occurs as indicated above (eq 1). The hydrogen is lost after rearrangement by some unknown mechanism. It does not lead to significant amounts of hydrogenated indene but apparently produces hydrogen. The change in the product in going from THF to ether can be rationalized in terms of stabilization of ion pairs by THF. In ether ions will be more poorly solvated and can, therefore, be more reactive. It should be noted, however, that firm conclusions cannot be drawn because (1) the reaction mixture in ether is heterogeneous and (2) the transition state structure for hydrogen loss from radical anion or dianion is not known.

Reduction of 1,1-diphenylindene or 1-methyl-1-phenylindene in THF produces rearranged indene. In these cases initial electron transfer is more difficult and sodium–potassium alloy is necessary to add an electron to the styrene-type π electrophore. The rearranged radical anion, *e.g.*, V, is also less stable than II and hydrogen loss again takes place.



It is interesting to note that cleavage of a phenyl group (forming 1-phenylindene) can compete with rearrangement when diphenylindene is reduced in THF. Although cleavage to form a phenyl radical or anion is not found with any of the closely related derivatives, it is found for diphenylindene not only in THF but also in dimethoxyethane and hexamethylphosphoramide. Cleavage of a phenyl group has also been described for 9,9-diphenylfluorene and triptycene.[25] In each of

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these cases a rather stable anion, *i.e.*, indenyl, fluorenyl, and a diphenylmethyl type, is formed and can account for the reaction.

The data make it quite clear that a phenyl group will migrate in preference to methyl. This is similar to the migratory aptitudes found for anion rearrangements from carbon to carbon[26] and for alkyl radical rearrangements.[27] The facility of phenyl migration appears to be a result of extra transition state bonding due to the π molecular orbitals of the phenyl group.[28] This phenyl migration appears to be the only example of a sigmatropic reaction catalyzed by solution phase electron transfer. The rearrangement observed for 1-methyl-1-phenylindene demonstrates that a 1,1-diphenyl structure is not necessary for rearrangement. This indicates that formation of a very stable *o*-quinodimethane radical anion is responsible for the facility of rearrangement.

Acknowledgment. This work was supported by a grant from the National Science Foundation.

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[26] H. E. Zimmerman in "Molecular Rearrangements," P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 391.

[27] C. Walling in ref 26, p 409.

[28] See N. F. Phelan, H. H. Jaffé, and M. Orchin, *J. Chem. Educ.*, 44, 626 (1967), and H. E. Zimmerman and A. Zweig, *J. Amer. Chem. Soc.*, **83**, 1196 (1961), for MO treatments of transition states in 1,2 rearrangements.

The Thermolysis of Substituted Indenes. Sigmatropic Phenyl and Hydrogen Migrations

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Abstract: 1,1,3-Triphenylindene, 1,1-diphenylindene, 1-methyl-1-phenylindene, and 1,3-diphenylindene rearrange at 250–300° *via* a 1,2-phenyl migration. The respective products formed are 1,2,3-triphenylindene, 2,3-diphenylindene, 3-methyl-2-phenylindene, and 2,3-diphenylindene. These reactions in diphenyl ether solution are kinetically of the first order. The rate constant for 1,1,3-triphenylindene rearrangement is unaffected by added acid, base, or free-radical scavengers. $\Delta S^{\ddagger}$ for this phenyl migration is -25 eu. Solvation of the transition state for rearrangement accounts for a portion of this very negative value as is indicated by the relative rates of rearrangement in solvent decalin (2.45), diphenyl ether (8.34), *o*-cresol (8.8), and dimethylformamide (16.5). In contrast, hydrogen rearrangement from the 1 to the 2 position of 1-phenylindene shows no solvent effect and $\Delta S^{\ddagger} = -2.3$ eu. Studies of hydrogen (deuterium) rearrangement in 1-deuterioindene, 1-phenylindene, and 1,3-diphenyl-1-deuterioindene at 150° allow estimation of phenyl substituent effects on sigmatropic hydrogen rearrangement. A 1-phenyl accelerates migration by about 130 and 3-phenyl by 6. Accelerative substituent effects on phenyl migration are similar: 1-phenyl (50), 3-phenyl (5), 1-methyl (8). These results are interpreted in terms of the transition state connecting reactant indene with an isoindene intermediate. The data reveal a migratory aptitude series hydrogen > phenyl > methyl which is determined by the more effective bridging capabilities of hydrogen compared to carbon.

A very large number of thermal sigmatropic reactions of neutral molecules have been discovered.[1] We report here on mechanistic aspects of indenyl substituent (hydrogen, phenyl) peregrinations.[2] Earlier work on this system was performed by Koelsch and Johnson[3] who isolated the products of thermal rearrangement over porous solids at 450–490°. They found that 1,1,3-triphenylindene produced 1,2,3-triphenylindene and that 1,3-, 1,2-, and 2,3-diphenylindene could be equilibrated.

Invisible thermal rearrangements of unsubstituted indene have been revealed by Alder,[4] Berson,[5] Isaacs,[6] and Roth.[7] These studies demonstrated that 1-deuterioindene produced 2-deuterioindene and that an isoindene intermediate could be trapped with maleic anhydride. The most comprehensive trapping study is that of Isaacs who showed that 2-deuterioindene produced a maleic anhydride adduct with ~90% of the deuterium intact on the bridge methylene. All of the results are consistent with Scheme I.[8]

Some of the most interesting discoveries of rearrangements in the indenyl system have been found in the study of fluxional organometallic molecules.[9] The first study of a σ-bonded indenyl metal compound appears to be the report that $(\pi\text{-}C_5H_5)Fe(CO)_2$ (σ-indenyl)

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[1] G. B. Gill, *Quart. Rev., Chem. Soc.*, 22, 338 (1968).

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[6] N. S. Isaacs, *Can. J. Chem.*, 44, 415 (1966).

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[8] Isaacs[6] found that the rate of disappearance of indene (**1**, R, R′ = H) was dependent on the maleic anhydride concentration. He was led to postulate rate enhancement *via* formation of a charge-transfer complex or a novel simultaneous hydrogen migration and attack by maleic anhydride. His data are *not*, however, inconsistent with Scheme I. Trapping must compete with return to indene. Therefore, the observed rate constant for disappearance of indene is $k_{\text{obsd}} = k_1[k_3(\text{MA})/(k_3(\text{MA}) + k_{-1} + k_2)]$. This equation demonstrates that k_{obsd} *should be* a function of (MA). The relative rate constants for trapping and return to indene can be evaluated as follows. Rearrangement of the above equation gives: $k_{\text{obsd}}/k_1 = (\text{MA})/[(\text{MA}) + (k_{-1} + k_2)/k_3]$. A good estimate of k_1 can be obtained by extrapolating Isaacs' rate *vs.* (MA) curve to slightly higher (MA) where $k_{\text{obsd}} = k_1$. This curve can then be fitted satisfactorily if $(k_{-1} + k_{-2})/k_3 = 0.5$. This value is consistent with the amount of scrambled deuterium in the trapped product if the expected isotope effect is considered.

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