

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 carbon²⁶ 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

(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.

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.

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(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

Larry L. Miller* and Rodney F. Boyer

Contribution from the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80521. Received February 13, 1970

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. ΔS^\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 Johnson³ 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

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

(2) Preliminary communication: L. L. Miller, R. Greisinger, and R. F. Boyer, *J. Amer. Chem. Soc.*, **91**, 1578 (1969).

(3) C. F. Koelsch and P. R. Johnson, *ibid.*, **65**, 567 (1943).

(4) K. Alder, F. Pascher, and H. Voight, *Chem. Ber.*, **75**, 1501 (1942).

(5) J. A. Berson and G. B. Aspelin, *Tetrahedron*, **20**, 2697 (1964).

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

(7) W. R. Roth, *Tetrahedron Lett.*, 1009 (1964).

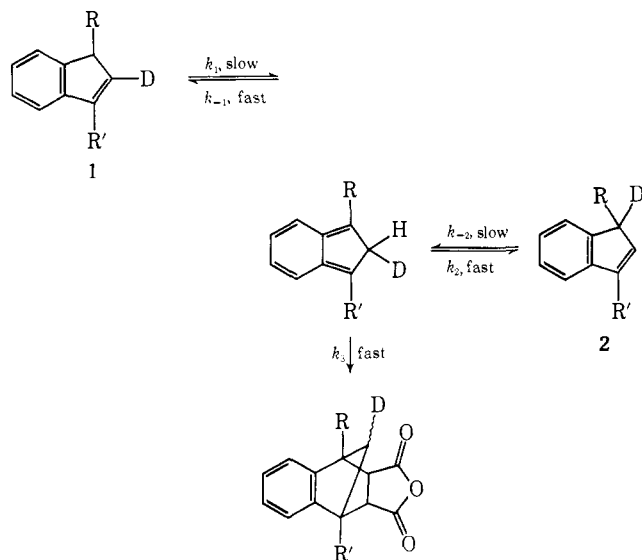
that of Isaacs who showed that 2-deuterioindene produced a maleic anhydride adduct with $\sim 90\%$ of the deuterium intact on the bridge methylene. All of the results are consistent with Scheme I.⁸

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 $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ (σ -indenyl)

(8) Isaacs⁶ 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.

(9) F. A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968).

Scheme I



does not exhibit fluxional behavior up to 70°. ¹⁰ Rakita and Davidson¹¹ observe that compounds of the type $(\text{CH}_3)_3\text{M}(\sigma\text{-indenyl})$ ($\text{M} = \text{Si}, \text{Ge},$ and Sn) are in fact fluxional, but data were not available in order to determine whether the mechanism involves 1,2- or 1,3-metal shifts. The fluxional behavior of bis(indenyl)mercury has been observed by Cotton.¹² He attributes this action to the available low lying valence-shell orbitals of mercury (6p or 5d) which could permit a 1,3 shift but which is not possible in $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\sigma\text{-indenyl})$ since iron has only one available valence-shell orbital which contains a single electron.

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, heptacosafuorotributylamine 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.

3,3,3-Triphenylpropanoic Acid. Only a 50% yield of this acid could be obtained using Hellerman's original procedure.¹³ By using the improved method of Denny, *et al.*,¹⁴ a 75% yield could be obtained. Recrystallization from 95% ethanol provided light tan crystals, mp 180–181° (lit.¹⁵ 180–181°). The nmr spectrum (CDCl_3) exhibits singlets at 6.30 (2 H), 2.78 (15 H), and 0.49 (1 H).¹⁵

3,3-Diphenyl-1-indanone. The procedure of Hellerman¹³ was followed to produce a quantitative yield of 3,3,3-triphenylpropanoyl chloride. The acid chloride in benzene with anhydrous AlCl_3 gave a 50% yield of this ketone, mp 132–133° (lit.¹⁶ 131–133°), after recrystallization from 95% ethanol. The nmr spectrum (CDCl_3)

showed singlets at 6.62 (2 H) and 2.8 (12 H). The ir spectrum (KBr) displayed peaks at 3.3, 5.38, and 12.5–14.0.

3,3-Diphenyl-1-indanol. The reduction of the above ketone was accomplished with LiAlH_4 . The procedure followed was that of Brown and Jackman.¹⁷ To avoid a gelatinous precipitate of hydroxides, the following work-up procedure was used: "the stirred mixture from n grams of LiAlH_4 is treated by successive dropwise addition of n ml of water, n ml of 15% sodium hydroxide solution and $3n$ ml of water. The granular precipitate formed is easy to filter and wash."¹⁸ After crystallization from benzene-Skellysolve H (1:2), fine white needles (mp 138°, lit.¹⁷ 131–132°) were obtained. Absorptions in the nmr spectrum (CDCl_3) were: broad singlet at 8.14 (1 H), multiplet at 7.0 (2 H), triplet at 4.82 (1 H) ($J = 6$ cps), and singlet at 2.78 (14 H).

1,1-Diphenylindene. The indanol was heated (1 hr) 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.¹⁷ 91–92°). The ir spectrum (KBr) had absorptions at 3.25, 6.25, 13.0, and 14.2. The nmr spectrum (CDCl_3) displayed singlets at 3.2 (2 H) and 2.75 (14 H). The mass spectrum showed prominent peaks at: 268 (100%), 267 (42%), 265 (18%), 252 (14%), 191 (24%), 189 (18%), 165 (10%), 133 (10%), and 126 (14%).

1,1,3-Triphenylindene. Two methods were used for the synthesis of this compound: that of Hodgkins and Hughes,¹⁹ and one method developed in these laboratories. The first method involved the reaction of dichlorodiphenylethylene and zinc dust. In the second procedure phenylmagnesium bromide was prepared by warming an ether solution of bromobenzene (6.24 g in 20 ml of ether) with magnesium (1 g). After all the magnesium was gone (30 min), an ether solution of 3,3-diphenylindanone (8 g in 100 ml) was added dropwise to the Grignard reagent. After a reflux period of 1 hr, the reaction mixture was quenched by the slow addition of ice-cold 10% H_2SO_4 . After ether extraction, drying, and concentration, a light brown oil was obtained. This oil was found to contain 1,1,3-triphenylindene and 1,3,3-triphenyl-1-indanol. If the oil was dissolved in an acetic acid solution of *p*-toluenesulfonic acid (1 g in 50 ml) and boiled for 1 hr, the alcohol was converted to the hydrocarbon. The oil was finally purified by placing it on a silica gel column and eluting with Skellysolve H. White prisms (5 g, 50%) were obtained with mp 135–136° (lit.¹⁹ 135–135.5°). Nmr absorptions (CCl_4) were observed at 3.18 (1 H) and 2.78 (19 H). The ultraviolet spectrum (95% ethanol) gave bands at λ_{max} 236 (ϵ 25,000) and λ_{max} 208 nm (ϵ 34,000). The mass spectrum recorded was: 344 (100%), 242 (57%), 267 (39%), 265 (43%), 163 (9%), and 78 (7.5%).

1,2,3-Triphenylindene. This hydrocarbon was prepared by the thermolysis of 1,1,3-triphenylindene.^{3,19} The light yellow product was purified by passing through a silica gel column, using Skellysolve H as the eluent. White crystals (0.85 g, 85%) were obtained, mp 134–136° (lit.³ 132–134°). A singlet at 4.8 (1 H) and a complex multiplet between 2.5 and 3.0 (19 H) comprised the nmr spectrum. Mass spectral peaks were: 344 (100%), 342 (55%), 267 (42%), 265 (40%), 163 (10%), and 78 (7.5%).

1,3-Diphenylindene. 3-Phenyl-1-indanone was prepared by refluxing a solution of cinnamic acid and anhydrous AlCl_3 in benzene.²⁰ The neutral fraction contained the ketone which was purified by crystallization from Skellysolve H, mp 78–79° (lit.²¹ 82–82.5°). Only an oil could be obtained from the reaction between phenylmagnesium bromide and 3-phenyl-1-indanone.²² The oil was purified by the use of a silica gel column, using Skellysolve H as eluent. This yielded white crystals, mp 69–70° (lit.²² 68–69°). Measurement by nmr (CCl_4) gave two doublets at 5.46 and 3.5 ($J = 2$ cps), each doublet integrating for one proton and a multiplet between 2.3 and 3.0 (14 H).

1-Deuterio-1,3-diphenylindene. 1,3-Diphenylindene (1 g) was dissolved in 10 ml of dry THF. It was added to a LiOD solution prepared by treating 0.1 g of lithium metal with 3 ml of D_2O . After a reflux time of 4 hr, DCl (1 ml, 35%) was added to neutralize the reaction. Ether extraction and finally column chromatography (silica gel-Skellysolve H) gave white needles, mp 68–69°. The nmr spectrum (CCl_4) had a multiplet at 2.3–3.0 (14 H), and a sharp sin-

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(11) P. E. Rakita and A. Davison, *Inorg. Chem.*, **8**, 1164 (1969).

(12) F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, **91**, 3178 (1969).

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(14) D. Denny, *et al.*, *ibid.*, **86**, 1119 (1964).

(15) W. H. Starnes, Jr., *ibid.*, **86**, 5604 (1964).

(16) A. G. Brook and J. B. Pierce, *Can. J. Chem.*, **42**, 298 (1964).

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

(18) L. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 584.

(19) J. E. Hodgkins and M. P. Hughes, *J. Org. Chem.*, **27**, 4191 (1962).

(20) C. F. Koelsch, *J. Amer. Chem. Soc.*, **65**, 59 (1943).

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

(22) C. F. Koelsch and P. R. Johnson, *J. Org. Chem.*, **6**, 534 (1941).

plet at 3.5 (1 H). Mass spectral peaks were: 269 (100%), 268 (54%), 266 (29%), 253 (29%), 254 (18%), 192 (32%), 190 (21%), 126.5 (21%), and 166 (11%).

3,3-Diphenylbutyric Acid. A procedure of Barltrop²³ was used to prepare this acid. The oil was purified by vacuum distillation, bp 150–170° (3 mm), and by removal of nonacidic impurities. After recrystallization from Skellysolve H, pure white crystals, mp 100–101° (lit.²³ 101°) (27%), were obtained.

3-Methyl-3-phenyl-1-indanone. Koelsch²⁰ has prepared this ketone by the AlCl₃ cyclization of the acid chloride of 3,3-diphenylbutyric acid. Following this procedure, a 50% yield of the ketone was realized. Spectral data were: ir bands at 3.3–3.4, 5.9; nmr absorptions (CCl₄) at 8.23 (3 H), singlet at 7.20 (2 H), and multiplet at 2.2–3.0 (9 H).

3-Methyl-3-phenyl-1-indanol. 3-Methyl-3-phenyl-1-indanone (3 g) was dissolved in 30 ml of dry ether and a solution of 0.7 g of LiAlH₄ in 30 ml of ether was slowly added to the ketone solution. After a reflux time of 3 hr the reaction mixture was quenched and worked up as in the preparation of 3,3-diphenyl-1-indanol. A 75% yield of the alcohol was obtained: mp (Skellysolve H) 126–127° (lit.²³ 125° (ethanol)); nmr spectrum (CCl₄) singlet at 8.33 (3 H), multiplet centered at 7.55 (2 H), triplet at 4.76 (1 H), and a multiplet centered at 7.75 (9 H).

1-Methyl-1-phenylindene. This hydrocarbon was prepared by the dehydration of 3-methyl-3-phenyl-1-indanol. The alcohol, 1.5 g, 20 ml of acetic acid, and 0.1 g of *p*-toluenesulfonic acid were heated to reflux for 1 hr. This reaction mixture was cooled, poured into 50 ml of ice water, and extracted with ether. The ether layer was washed with 10% sodium carbonate until all acetic acid was removed. After drying and concentrating the ether solution, an oil remained (0.8 g, 60%). Prominent mass spectral peaks included: parent 206 (25%), 191 (28%), 165 (47%), 128 (100%), 77 (62%), and 63 (98%). The nmr spectrum (CCl₄) showed a singlet at 8.35 (3 H), two doublets centered at 3.45 (2 H, *J* = 6 cps), and a singlet at 2.85 (9 H).

Anal. Calcd for C₁₆H₁₄: C, 93.20; H, 6.80. Found: C, 93.46; H, 6.91.

3-Phenyl-1-indanol. 3-Phenyl-1-indanone (2.4 g) was reduced with LiAlH₄ (0.75 g). A white solid, mp 95° (lit.²³ 94.5–95°), was produced.

1-Phenylindene. This olefin was prepared by heating 2.0 g of 3-phenyl-1-indanol in an acetic acid solution of *p*-toluenesulfonic acid (0.5 g in 25 ml). A light oil (1 g) was purified on a silica gel column (eluent: Skellysolve H). The nmr spectrum (CCl₄) consisted of a triplet at 5.48 (1 H) (*J* = 2 cps), two pairs of doublets centered at 3.33 (2 H) (*J* = 2 cps), and a multiplet centered at 2.88 (9 H).²¹

3-Phenylindene. By treating 1-phenylindene with triethylamine, an 85% yield of 3-phenylindene was obtained.²¹ The product was an oil, bp 117–119° (0.49 mm) (lit.²⁴ 118–119°, 0.45 mm). The nmr spectrum (CCl₄) showed a doublet at 6.5 (2 H), a triplet at 3.50 (1 H), and a multiplet centered at 2.6 (9 H).²⁰

2,3-Diphenylpropanoic Acid. This acid was prepared following the procedure in *Organic Syntheses*.²⁵ The acid was prepared in 80% yield, mp 95–96° (lit.²⁵ 95.5–96.5°). The nmr spectrum (CDCl₃) showed a complex multiplet from 6.0 to 7.2 (3 H) and two singlets at 2.95 and 2.80 (10 H).

2-Phenyl-1-indanone. The synthesis of this compound was achieved by the AlCl₃ catalyzed cyclization of 2,3-diphenylpropanoyl chloride.²⁶ The acid chloride was prepared by the use of PCl₅.²² The ketone, mp 77° (lit.²² 77–78°), was purified by recrystallization from Skellysolve H. Two complex multiplets at 6.2–7.0 (3 H) and 2.2–3.0 (9 H) comprise the nmr spectrum. The ir spectrum showed absorptions at 3.25, 5.85, and 13.2–14.3.

3-Methyl-2-phenylindene. Methylmagnesium iodide and 2-phenyl-1-indanone were treated in ether. The product was purified on a silica gel column using Skellysolve H as the eluent. In fractions 1–3, yellow crystals were obtained, mp 80° (lit.²⁷ 80°). This indene has an nmr spectrum similar to that previously reported.²⁸

1,1,3-Triphenylindene Thermolysis. This hydrocarbon (1 g) was dissolved in 7 ml of diphenyl ether and sealed in a 15 × 2 mm

Pyrex tube. The tube was placed in a constant temperature bath (240°) for 15 hr. The solvent was removed by vacuum distillation leaving a light yellow residue which was further purified on a silica gel column. Eluting with Skellysolve H and collecting 200-ml fractions, crystals were obtained in fractions 4–8. An 85% yield of white prisms (mp 134–136°) was obtained. An examination of the nmr spectrum and mass spectrum suggested 1,2,3-triphenylindene (mp lit.¹⁹ 132–134°).

1,1-Diphenylindene Thermolysis. Diphenylindene (1 g) was sealed in a test tube with 5 ml of diphenyl ether. After a thermolysis time of 10 hr at 280°, the reaction product was isolated by distilling the solvent. The light yellow residue could be purified by recrystallizing from 95% ethanol. The pure white needles, 0.9 g (90%), mp 110°, were found to be identical with a sample of 2,3-diphenylindene (mp lit.²⁹ 108°) from Na–K reduction of 1,1-diphenylindene. Gas chromatographic analysis showed only two components in the reaction mixture, 10% 1,1-diphenylindene and 90% 2,3-diphenylindene.

1-Methyl-1-phenylindene Thermolysis. The following are sealed in a test tube: 1 g of 1-methyl-1-phenylindene and 5 ml of diphenyl ether. After 20 hr at 300°, the tube was broken open and worked up as described before. The remaining light yellow oil was chromatographed on silica gel (Skellysolve H). The nmr spectrum showed a triplet at 7.75 (3 H) (*J* = 2 cps), a quartet at 6.35 (2 H) (*J* = 2 cps), and a multiplet at 2.7 (9 H). This was in exact agreement with an authentic sample of 3-methyl-2-phenylindene which was prepared as described above.

1,3-Diphenylindene Thermolysis. Into a test tube was sealed 1 g of 1,3-diphenylindene. This tube was placed in a constant temperature bath at 300° for 12 hr. A light yellow solid remained after work-up. The solid could be crystallized from 95% ethanol which yielded 87% of 2,3-diphenylindene, mp 110°.

1,2-Diphenylindene Thermolysis. The olefin (1 g) was dissolved in 6 ml of diphenyl ether and sealed in a test tube. After 20 hr at 160°, the tube was opened and the solvent distilled, leaving a light yellow oil. Upon dissolving this oil in a minimum amount of warm 95% ethanol, light yellow crystals formed upon standing, mp 110°. The product was 2,3-diphenylindene in 90% yield.

1-Phenylindene Thermolysis. A tube containing 1 g of 1-phenylindene and 5 ml of diphenyl ether was sealed and placed in a constant temperature bath at 150°. After 10 hr the tube was withdrawn and opened. The solvent and product could not be separated by distillation so gas chromatography was used to identify the products. The product was shown to be 3-phenylindene in 90% yield. If *tert*-butylbenzene was used as the solvent, the product could be isolated from the reaction mixture. Again the product was 3-phenylindene in 90% yield.

1-Deuterio-1,3-diphenylindene Thermolysis. Into a test tube was sealed 1 g of 1-deuterio-1,3-diphenylindene and 5 ml of diphenyl ether. The tube was placed in a bath at 150° for 10 hr. After distillation of the solvent a yellow residue remained. This residue could be purified by recrystallization from Skellysolve H, yielding white needles, mp 68–69°. Two products could be detected by nmr: 1-deuterio-1,3-diphenylindene and 2-deuterio-1,3-diphenylindene.

Thermolysis of 1-Deuterio-1,3-diphenylindene and 1-Phenylindene. A test tube was sealed containing 0.3 g of 1-phenylindene, 0.3 g of 1-deuterio-1,3-diphenylindene, and 2 ml of *tert*-butylbenzene. The tube was placed in a constant temperature bath for 6 hr at 160°. The tube was opened and the solvent distilled under vacuum leaving a dark oil. The residue was chromatographed on a silica gel column using Skellysolve H as eluent. An oil appeared in fractions 5–7 which was identified by its nmr spectrum as 3-phenylindene. Mass spectroscopic studies showed that no deuterium was present. White crystals in fractions 10 and 11 were shown by nmr to be 2-deuterio-1,3-diphenylindene.

Thermolysis of 1,1,3-Triphenylindene and Hydroquinone. Hydroquinone (0.25 g) was sealed in a test tube with 5 ml of diphenyl ether and 0.25 g of 1,1,3-triphenylindene. It was placed in a constant temperature bath at 240° for 6.5 hr. After this time the tube was opened, the solvent was distilled, and the residue placed on a silica gel column. Using Skellysolve H as eluent, white crystals, mp 135°, could be obtained in fractions 2–3. The yield of 1,2,3-triphenylindene was 0.20 g, 80%.

Kinetic Studies of Substituted Indene Thermolysis. The progress of each reaction could be conveniently followed by the use of nuclear magnetic resonance. Two techniques could be used: (a) following

(23) J. A. Barltrop, *J. Chem. Soc.*, 2928 (1956).

(24) B. Weinstein, *J. Org. Chem.*, 26, 4161 (1961).

(25) C. R. Hauser and W. R. Dunnivant, *Org. Syn.*, 40, 38 (1960).

(26) N. Campbell and E. Ciganek, *J. Chem. Soc.*, 3834 (1946).

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

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

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

Table I. Kinetic Data for Thermolysis of 1,1,3-Triphenylindene in Different Solvents at 230°

Reaction time, sec	Integration			
	Product ^b		Standard ^c	
1,800 ^a	0.2	0.3 ^d	4.8	7.0 ^d
3,600	0.4	0.5	4.9	6.5
5,400	0.5	0.7	4.5	7.8
7,200	0.6	1.0	4.2	7.0
9,000	0.7	1.1	4.0	6.5
3,600 ^e	2.4 ^f		0.3	
7,200	2.5		0.5	
10,800	2.1		0.6	
14,400	2.2		0.9	
18,000	1.7		1.0	

^a Solvent is diphenyl ether. ^b Reactant concentration 0.2 M. ^c Toluene concentration 0.2 M. ^d Second run under same conditions. ^e Solvent is decalin. ^f Reactant concentration 0.20 M.

Table II. Kinetic Data for Thermolysis of 1-Phenylindene at Several Temperatures in Diphenyl Ether

Reaction time, sec	Integration	
	Reactant	Product
1,800 ^a	13.5	7.0
3,600	12.0	12.0
5,400	5.5	8.5
7,200	5.0	15.0
9,000	6.0	24.0
10,800	5.0	24.0
1,800 ^b	23.0	8.5
5,400	13.5	16.0
12,600	11.5	26.2
16,200	8.0	30.0
7,200 ^c	17.0	5.0
10,800	16.0	6.0
14,400	11.0	8.0
21,600	12.0	14.0
28,800	10.5	16.0
36,000	10.0	19.0
46,800	7.5	20.0

^a Temperature is 160°, reactant concentration 0.25 M. ^b Temperature is 150°, reactant concentration 0.25 M. ^c Temperature is 140°, reactant concentration 0.25 M.

the appearance of a product proton *vs.* some internal standard or (b) comparing the rate of appearance of a product proton *vs.* the disappearance of a reactant proton. Each peak area was carefully integrated five times and an average integration was calculated. Diphenyl ether was a very satisfactory solvent as it had a high boiling point (260°), and all of the indenenes were very soluble in it. Runs were also made in decalin, nitrobenzene, *o*-cresol, and dimethylformamide. Concentrations of approximately 0.2 M were required for the nmr studies. Because of the limited solubility of the indenenes in the final three solvents listed, it was necessary to use the infinity concentration of the product as the initial concentration of reactant. Pyrex test tubes of size 10 × 75 mm or nmr tubes used for the kinetic runs were cleaned thoroughly with soap and water, finally rinsed with distilled water and acetone, and dried for several hours in an oven at 120°. Hydrogen rearrangements were strongly catalyzed by base; however, no rate change was noted if the cleaning procedure included rinsing with dilute hydrochloric acid.

Two methods were used for the kinetic runs: (a) 1 ml of the stock solution of indene was added to each of 6–8 test tubes and these were sealed and immersed in a wire basket into the heated oil. Tubes were then withdrawn for analysis at certain intervals, or (b) 0.5 ml of the solution was sealed in a single nmr tube and this tube was used throughout the run by withdrawing it from the bath at preselected intervals for analysis. It was found that rates determined from either method did not vary more than the experimental error in either. The nmr peaks monitored in diphenyl ether were: 1-phenylindene, 6.5 product, 5.5 reactant; 1-deuterio-1,3-diphenylindene, 5.46 product; 1,3-diphenylindene, 6.12 product; 1-methyl-1-phenylindene, 7.75 product, 8.53 reactant; 1,1-diphenylindene, 6.12 product; 1,1,3-triphenylindene, 4.8 product.

The temperature of the bath was controlled with a Thermistemp Temperature Controller, Model 63RA, Yellow Springs Instrument Co. This model was equipped with a probe for use between 200 and 500°F. Between 100 and 200° the temperature could be controlled to ±0.5°. Between 200 and 300° the temperature varied ±1°.

All reactions were followed to at least 80% completion or about 2.5 half-lives. In all cases straight lines were obtained from plots of $\log C_0/C$ *vs.* time, where C_0 is the initial concentration of reactant, and C is the concentration of the reactant at any time t . All calculations were carried out using a CDC 6400 computer. Input for the program consisted of the temperature, initial concentration of reactant and standard, and the nmr integration of the peak area. The output included the rate constants, first-order rate plots, an Arrhenius plot, E_a , ΔH^\ddagger , and ΔS^\ddagger by the least-squares method. Sample data are found in Tables I and II.

Results

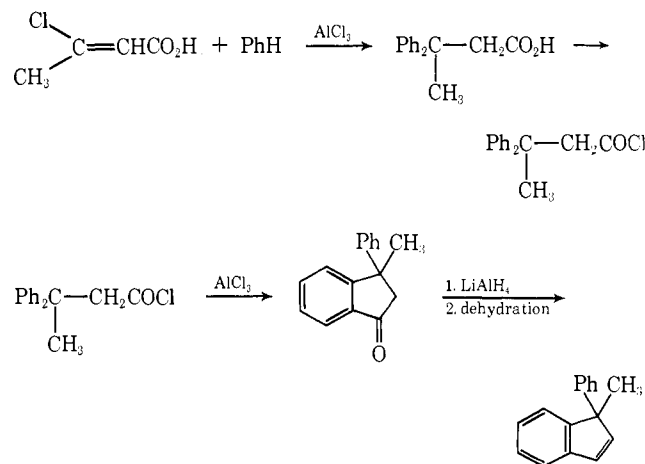
The substituted indenenes listed in Table III were prepared and thermolyzed in sealed tubes with diphenyl ether solvent. The reactants are with two exceptions all

Table III. Products from Thermolysis of Substituted Indenes

Reactant	T , °C	Product
1,1,3-Triphenylindene	230	1,2,3-Triphenylindene
1,1-Diphenylindene	260	2,3-Diphenylindene
1-Methyl-1-phenylindene	300	3-Methyl-2-phenylindene
1,3-Diphenylindene	300	2,3-Diphenylindene
1-Deuterio-1,3-diphenylindene	150	2-Deuterio-1,3-diphenylindene
1-Phenylindene	150	3-Phenylindene
1,2-Diphenylindene	160	2,3-Diphenylindene

known compounds and were prepared by literature methods. In some cases new spectroscopic evidence confirmed previous assignments of structure. The previously uncharacterized 1-deuterio-1,3-diphenylindene was prepared by refluxing 1,3-diphenylindene in LiOD-D₂O for 4 hr. The nmr spectrum demonstrated essentially complete deuteration at the 1 position and no deuteration at 2. Thermolysis produced a mixture of 1- and 2-deuterio compounds.

1-Methyl-1-phenylindene was prepared *via* the following scheme. The thermolysis product mixtures



were examined by nmr and glc, and in general it was demonstrated that only one product was formed in very high yield. Work-up of these mixtures then allowed a more careful characterization of the product. In several cases isomeric products could have formed, but the product with methyl or phenyl substituted on the double

bond predominated to a very large degree, *e.g.*, 1,1-diphenylindene produced only 2,3-diphenylindene and undetectable amounts of 1,2-diphenylindene. This result varies from that found under more vigorous, heterogeneous conditions by Koelsch and Johnson. Products resulting from exchange of groups between molecules could not be detected. In a crossover experiment in which 1-phenylindene and 1-deuterio-1,3-diphenylindene were thermolyzed together, no 3-phenylindene with deuterium labeling was found upon nmr and mass spectral studies of the products. Such a result is consistent with an intramolecular rearrangement of hydrogen and deuterium. In regard to phenyl migration such an experiment is dependent upon synthesis of properly labeled molecules, a task which at this point has not been accomplished.

The rate studies employed an nmr assay which compared the integrated area of a product peak with that of an internal standard. Least-squares computer analysis provided the first-order rate constants in Tables IV–VII.

Table IV. Rate Constants and Activation Parameters for Thermolysis of 1-Phenylindene in Diphenyl Ether

T , °C	k , sec ⁻¹	ΔS^\ddagger , ^a eu	E_a , ^a kcal/mol
160	$1.17 \times 10^{-4} \pm 0.01$		
150	$5.75 \times 10^{-5} \pm 0.01$	-2.3	33.2
140	$1.81 \times 10^{-5} \pm 0.008$		
160 ^b	1.1×10^{-4}		

^a At an average temperature of 150°. ^b Decalin solvent.

Table V. Rate Constants and Activation Parameters for Thermolysis of 1,1-Diphenylindene in Diphenyl Ether

T , °C	k , sec ⁻¹	ΔS^\ddagger , ^a eu	E_a , ^a kcal/mol
280	$2.13 \times 10^{-4} \pm 0.03$		
270	$1.48 \times 10^{-4} \pm 0.02$	-27.2	28.3
260	$9.76 \times 10^{-5} \pm 0.01$		
250	$4.75 \times 10^{-5} \pm 0.02$		

^a An average temperature of 265°.

Table VI. Rate Constants and Activation Parameters for Thermolysis of 1,1,3-Triphenylindene

Solvent	T , °C	$10^5 k$, sec ⁻¹	ΔS^\ddagger , ^a eu	E_a , ^a kcal/mol
Diphenyl ether	220	4.74 ± 0.01		
	225	6.12 ± 0.01	-25.1	27.7
	230	8.34 ± 0.005		
	236	11.1 ± 0.02		
Decalin	230	2.45		
Nitrobenzene ^b	230	6		
<i>o</i> -Cresol	230	8.8		
Dimethylformamide	230	16.5		

^a At 227°. ^b Decomposition occurred.

The indicated errors are deviations for the typical run cited. The Arrhenius plots appeared linear and activation parameters are included for three rearrangements in diphenyl ether. The 1,1,3-triphenylindene rate constant was independent of indene concentration and unaffected by added hydroquinone, quinoline, or trichloroacetic acid or by degassing. Phenyl rearrangement was also not catalyzed by decomposing benzoyl peroxide at 100°.

Table VII. Rate Constants for Indene Isomerization in Diphenyl Ether Solution

Reactant	T , °C	$10^5 k$, sec ⁻¹	Migrating group
1,1,3-Triphenylindene	228	7.0	Phenyl
	228	7.2 ^a	
	228	7.5 ^b	
	228	6.9 ^c	
1,1-Diphenylindene	280	20.0	Phenyl
1-Methyl-1-phenylindene	300	8.0	Phenyl
1,3-Diphenylindene	300	6.2	Phenyl
1-Deuterioindene	220	7.6 ^d	Deuterium
1-Phenylindene	150	5.7	Hydrogen
1,3-Diphenyl-1-deuterioindene	150	9.0	Deuterium

^a 0.25 *M* trichloroacetic acid present. ^b 0.15 *M* quinoline present. ^c Degassed by three freeze-thaw cycles. ^d Gas-phase data from ref 8.

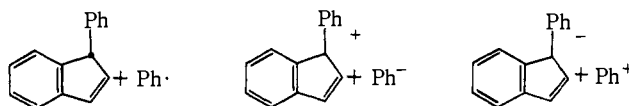
Discussion

Previous studies of the rearrangement of deuterated indene^{4–7} have rather firmly established the validity of Scheme I. 1-Phenylindene and 1-deuterio-1,3-diphenylindene appear to follow the same mechanism. The expected products are formed and the entropy of activation is of the expected magnitude.³⁰ McLean and Haynes³¹ found $\Delta S^\ddagger = -10$ eu for the (1,5)-hydrogen rearrangement of 1-methylcyclopentadiene and $\Delta S^\ddagger = -4$ eu for 1,2-dimethylcyclopentadiene and for 5*H*-perdeuteriocyclopentadiene, $\Delta S^\ddagger = -12$ eu.⁷ Only slightly more negative ($\Delta S^\ddagger \approx -13$ eu) values are found for a variety of acyclic 1,5-hydrogen shifts³² which should require a considerable confinement of the carbon chain.

A crossover experiment was performed by heating an equimolar mixture of 1-deuterio-1,3-diphenylindene and 1-phenylindene. No deuterated 1-phenylindene was formed and all the 1,3-diphenylindene was mono-deuterated. Since these two compounds rearrange at essentially the same rate, it is clear that hydrogen rearrangement is intramolecular. It is concluded that hydrogen rearranges in all of these cases *via* a true sigmatropic mechanism.

Phenyl migrations of the type encountered in this study have not been previously investigated. We have found that the rearrangement of phenyl is first order and specific for migration to the 2 position. It is not catalyzed by acid or base or free radicals. The rearrangement products and rate are not affected by the radical scavengers oxygen and hydroquinone. These data exclude a variety of catalytic, bimolecular, and chain mechanisms. It also seems improbable that intermolecular cleavage-recombination mechanisms are involved.

Three types of cleavage products can be imagined. Formation of a free phenyl radical seems impossible



because (1) the bond strength to be overcome must be greater than the observed E_a , (2) ΔS^\ddagger should be positive, not negative, (3) recombination should take place at

(30) K. W. Egger, *J. Amer. Chem. Soc.*, **89**, 3688 (1967).

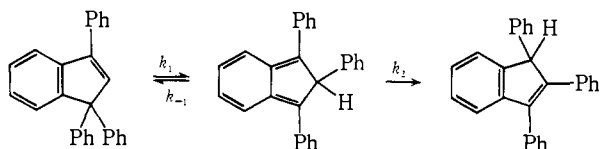
(31) S. McLean and P. Haynes, *Tetrahedron Lett.*, 2385 (1964).

(32) H. F. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969).

C-3 as well as C-2, and this is not observed, and (4) phenyl radicals should be trapped with radical scavengers.

Formation of an antiaromatic indenyl cation and a phenyl anion is clearly impossible. Formation of an indenyl anion is much better since it is relatively stable. It is known, however, that phenyl trifluoromethylsulfonate will not solvolyze even in ionizing solvents at 150°. ³³ This means that phenyl cations will not form even with the best leaving anion yet discovered. The third intermolecular possibility is therefore ruled out. The intramolecular counterparts (ion or radical pairs) of these are less readily dispensed with, but seem improbable for the reasons cited above.

All of the data presented are consistent with a concerted, sigmatropic shift. In terms of this mechanism, the relative stabilities of isoindene and reactant demand



that k_{-1} must be greater than k_1 . We find that hydrogen migration occurs much faster than phenyl so that k_2 must be greater than k_{-1} . k_1 must then be rate determining and the isoindene intermediate must proceed to product without reverting to reactant.

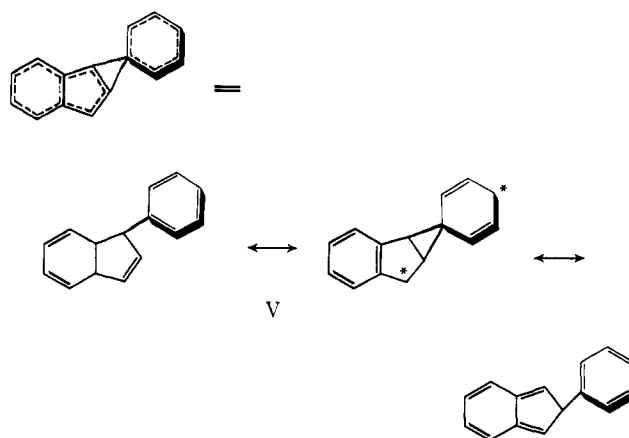
Further kinetic studies have, however, unearthed two fascinating pieces of data which must still be rationalized by this mechanism. The $\Delta S^\ddagger \approx -27$ eu is quite unexpected. Even allowing for considerable error, this is very different from values found for sigmatropic hydrogen migrations. A related phenomenon is the observed dependence of the rate on the solvent. The rate of hydrogen migration in 1-phenylindene is not affected by changing the solvent from decalin to diphenyl ether and similar results have been found for other 1,5-hydrogen shifts. ^{34,35} Phenyl migrations, contrastingly, show a considerable solvent dependence (Table VI). Because of the nonpolar nature of the solvents and the high temperatures employed, the origin of the effects is not certain. It is clear, however, that solvation of the rearrangement transition state is important and that orientation of solvent molecules accounts for a large fraction of the negative entropy of activation. A transition state which accommodates the data is V. This species would clearly have different properties than the proposed transition state for hydrogen migration and might have dipolar character. It might, in fact, be considered a homoconjugated diradical or zwitterion. ³⁶ Dipolar character would call for solvation of charge and the combination of a specific orientation for the bridging phenyl and polar solvation would nicely rationalize the ΔS^\ddagger value. It is not clear, however, that this picture is consistent with the substituent effects at the 1 and 3 positions. Further studies will be needed to reveal the detailed transition state structure.

(33) T. M. Su, W. F. Sliwinski, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 5387 (1969).

(34) A. P. ter Borg and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **82**, 741 (1965); *ibid.*, **88**, 270 (1969).

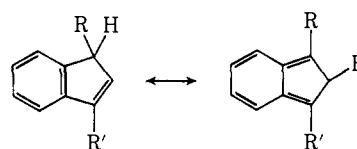
(35) R. W. Murray and W. L. Kaplan, *J. Amer. Chem. Soc.*, **88**, 3527 (1966).

(36) D. J. Cram and A. Ratajczak, *ibid.*, **90**, 2198 (1968).



A comparison of the rates of rearrangement of 1-deuterioindene, 1-phenylindene, and 1-deuterio-1,3-diphenylindene allows estimates of phenyl substituent effects on sigmatropic deuterium rearrangements. The rate constant for conversion of **2** to **1** (Scheme I) via deuterium migration can be expressed as $k_{\text{obsd}}^D = k_{-2} [k_{-1}/(k_{-1} + k_2)]$. For a valid estimation of substituent effects, it is then necessary to extract approximate values of k_{-2} using this expression. ³⁷ At 150° it is assumed that $k_H/k_D = 3$ for hydrogen migrations. Therefore, for 1-deuterio-1,3-diphenylindene, $k_{-2}^D = 9.0 \times 10^{-5} \times 4/3 = 1.2 \times 10^{-4} \text{ sec}^{-1}$. For the hypothetical 1-deuterio-1-phenylindene it will be assumed that $k_{-1} \gg k_2$. Using k_{obsd} for 1-phenylindene, $k_{-2}^D = 1/3 k_{-2}^H = k_{\text{obsd}} = 1.9 \times 10^{-5} \text{ sec}^{-1}$. Comparing k_{-2}^D for these two compounds then gives a rate acceleration of six to a 3-phenyl substituent.

Using the assumption $k_{-1} \gg k_2$ again for 1-phenylindene, $k_H/k_D = 2$ at 220° and extrapolating k_{obsd} to 220°, $k_{-2} = 6.5 \times 10^{-3}$. For 1-deuterioindene at 220° ³⁷ assuming $k_{-1}/k_2 = 2k_{-2} = 7.6 \times 10^{-5} \times 2/3 = 5.1 \times 10^{-5}$. The rate acceleration due to a 1-phenyl is ~ 130 . These rate differences can be largely rationalized in terms of the structures in Scheme I and two contributing structures for the transition state for k_{-2} . The



3-phenyl ($R' = \text{Ph}$) is conjugated with the π system in the reactant and in both transition state structures and, therefore, has minor effects upon the rate. The 1-phenyl ($R = \text{Ph}$), however, is not conjugated in the reactant, but is conjugated in one of the transition state contributors accounting for the larger rate effect. There are undoubtedly other steric and electronic effects in both the 3- and the 1-phenyl accelerations, but it seems unprofitable to attempt further interpretation. Phenyl and methyl substituent effects on (1,5)-sigmatropic hydrogen shifts have been studied by Kloosterziel and coworkers. ³⁴ It is found that 7-phenyl accelerates the hydrogen migration in cycloheptatriene by a factor

(37) A good model for these isotope effects is not available, but at these temperatures and considering that the major effect will be loss of a C-H bending mode in the transition state, they should not be large. Although the k_{-2} values obtained in this way are crude, they are still more meaningful than k_{obsd} comparisons.

of about 20 (assuming $k_H/k_D = 3$ at 136.5°). 7-Methyl, 3-phenyl, and 1-phenyl groups had only very small effects on the rate. This is consistent with our findings except that rather larger substituent effects are found in the indenyl system. A geometrically more closely related reaction is the rearrangement of methylcyclopentadienes. Quantitative data are available only for a few compounds but it is apparent that a 5-methyl accelerates rearrangement.³¹ In all three cases (indene, cycloheptatriene, and cyclopentadiene), the most important effect appears to be an acceleration by carbon substituents located at the migration origin.

Extrapolation of the rates of 1,1,3-triphenylindene and 1,1-diphenylindene to 300° allows an estimate of several substituent effects. Compared to hydrogen: (1) a 1-phenyl group accelerates by a factor of 50, (2) a 3-phenyl accelerates by 5, (3) a 1-methyl accelerates by 8. Considering the approximations used to estimate substituent effects on hydrogen migration, it appears that the effects on phenyl and hydrogen rearrangement are quite similar.

The kinetic and product studies demonstrate that hydrogen migrates to the exclusion of phenyl which in turn is much preferred over methyl. This order appears to be primarily due to transition state stabilization by the migrating group rather than by the group that remains behind. Hydrogen rearrangement in 1-phenylindene and phenyl migration in 1,1-diphenylindene involve different migrating groups but the same nonmigrating moiety, and the hydrogen migrates much faster than phenyl. Since this system is the only example of a sigmatropic phenyl shift it is not clear that this order will always be found. There are, however, numerous examples where hydrogen migration is preferred to

alkyl.^{30,31,34} The high activation energy for methyl migrations, for example, explains why an alternate rearrangement pathway is followed for 7,7-dimethylcycloheptatriene thermolysis.³³ There would appear to be two important factors which could determine the migratory aptitude of a group or atom. They are: (1) the ability to form a "bridged" transition state and (2) the nature of the highest occupied molecular orbital (HOMO) about which the group is migrating.³⁹ In the present case one needs to consider a transition state model composed of an indenyl radical complexed with the migrating group. A Huckel calculation indicates that the HOMO of the indenyl radical is nodal at C-2. It seems imperative to utilize a suprafacial³⁹ migration and this will involve simultaneous overlap of the migrating group with a "+ lobe" at C-1 and a "node" at C-2. There is no rule³⁹ for this case, but the problem can be treated by second-order perturbation theory. For the present, both hydrogen and carbon (1,5)-group migrations occur under proper conditions and should be considered "allowed." The relative ease of hydrogen rearrangement seems to be due to its ability to bridge, *i.e.*, a bridged hydrogen is more stable relative to its unbridged precursor than is a bridged carbon relative to its precursor. A phenyl can partially overcome the reluctance of carbon to bridge by attaining a rather different and strongly solvated transition state. A characteristic of other phenyl migrations is utilization of low lying π orbitals not available to alkyl groups. This may also occur here *via* a transition state like V which would make ΔH^\ddagger and ΔS^\ddagger more negative.

(38) J. A. Berson and M. R. Willcott, *J. Amer. Chem. Soc.*, **88**, 2494 (1966).

(39) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 2511 (1965).