Hz)] but entirely consistent with the assigned structure. The electronic spectrum [$\lambda_{max}^{CH_3CN}$ 228 nm (ϵ 14,000), 256 (13,700), 261 (12,900), 293 (11,100), 317 (8800), 550 (1800)] resembled that of other annelated tropylium ions.[4]

Attempts to convert **5** into **1** by treatment with trimethylamine according to the method of Dauben and Bertelli[5] gave a complex mixture of products, but no evidence for the production of **1** could be adduced. Reaction of **5** with a second mole of trityl fluoroborate did not lead to the dication, the nmr spectrum remaining virtually unchanged.

Experimental Section

The nmr spectra were run on a Varian HA-100 spectrometer with TMS as internal standard and are reported in τ units. Electronic spectra were recorded on a Unicam SP 800 spectrophotometer. Ir spectra were recorded on a Unicam SP 200 spectrometer. Mass spectra were taken with an AEI MS12 spectrometer at 70 eV.

Preparation of Mixtures of 1,7- (3) and 1,11-Dihydrobenzo-[1,2:4,5]dicycloheptene (4).—The hydrocarbon **2** (4.28 g, 20 mmol) and N-bromosuccinimide (12.24 g, 80 mmol) were suspended in CCl₄ (300 ml), benzoyl peroxide (20 mg) was added, and the mixture heated under reflux until all of the N-bromosuccinimide had reacted (~3 hr). The resulting mixture was filtered to remove the succinimide, and evaporation of the solvent from the filtrate gave a glass (13.4 g). The nmr spectrum (CCl₄) showed signals at τ 2.4–2.6 (m, aromatic), 4.3–4.7 (b, s, benzylic), and 7.2–8.4 (aliphatic). The glass was dissolved in dimethylformamide (40 ml), 1,5-diazabicyclo[5.4.0]undeca-5-ene (10 ml), was added, and the mixture stirred at 80° for 3 hr. The mixture was then poured into water, 50 ml of 5 N HCl was added, and the mixture was extracted with ether (3 × 100 ml). The ethereal extracts were washed with water (3 × 50 ml), saturated NaCl solution (1 × 50 ml), and dried (Na₂SO₄). The solvent was removed by evaporation and the resulting dark solid was chromatographed on silica gel (90 g), eluting with petroleum ether. A white crystalline material was obtained (1.75 g) which slowly turned yellow on standing. A number of purification procedures were investigated. Six recrystallizations of the material from ethanol gave white plates (45 mg) which consisted of a 4:1 mixture of **3** and **4**: mass spectra m/e 206; ir (KBr) 1500, 1430, 1370, 910, 800, 690 cm⁻¹; nmr (CDCl₃) 6.98 (d, $J \approx$ 7 Hz), 4.25 (m, $J \approx$ 7, 9.5 Hz), 3.96 (dd, $J \approx$ 5.5, 9.5 Hz), 3.58 (dd, $J \approx$ 5.5, 12 Hz), 3.06 (s), 2.96 (d, $J \approx$ 12 Hz), 2.92 (s), 2.15 (s); λ_{max}^{EtOH} 240 nm (ϵ 8000), 311 (14,000).

Anal. Calcd for C₁₆H₁₄: C, 93.16; H, 6.84. Found: C, 93.09; H, 6.83.

(4) See G. Naville, H. Strauss, and E. Heilbronner, *Helv. Chim. Acta,* **43**, 1221 (1960).

(5) H. J. Dauben and D. J. Bertelli, *J. Amer. Chem. Soc.,* **83**, 4659 (1961).

Glc (Carbowax 20M, 256°) of the crystalline material (500 mg) gave a 1:1 mixture (55 mg) of **3** and **4**. Column chromatography on 20% AgNO₃-impregnated alumina (80 g)[6] of the crystalline material (800 mg), eluting with ether–benzene, gave a 1:2 mixture (85 mg) of **3** and **4**. A crystalline tetrahydrobenzo-[1,2:3,4]dicycloheptene fraction (180 mg) was also isolated in this separation.

Preparation of 1H-Benzo[1,2:4,5]dicycloheptenium Tetrafluoroborate(1−) (5).—A mixture (1:2) of the olefins **3** and **4** (25 mg, 0.12 mmol) was added to a solution of trityl fluoroborate (40 mg) in dry acetonitrile (10 ml) under dry N₂. The mixture was stirred until all of the olefin had dissolved (~1 hr), the solvent was removed *in vacuo*, and the residue was washed with dry ether (3 × 5 ml) to give **5** (30 mg, 0.10 mmol, 83%) as dark red needles, which decomposed on attempted mp determination: for nmr see discussion; for electronic spectrum, see discussion; ir (KBr), 1500, 1060, 920, 700 cm⁻¹.

Anal. Calcd for C₁₆H₁₃BF₄: C, 65.75; H, 4.78. Found: C, 65.77; H, 4.48.

Registry No.—**2**, 14314-88-6; **3**, 40682-46-0; **4**, 40682-47-1; **5**, 40674-83-7; N-bromosuccinimide, 128-08-5; trityl tetrafluoroborate, 340-02-6.

(6) See R. Wolovsky, *J. Amer. Chem. Soc.,* **87**, 3638 (1965).

Thermally Induced Side Chain to Ring Migrations in Aromatic Systems

JOHN M. PATTERSON,* NABEEL F. HAIDAR, CHYNG-YANN SHIUE, AND WALTER T. SMITH, JR.

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506

A number of organic molecules undergo rearrangements, by a variety of mechanistic pathways in which a group migrates from a side chain in an aromatic system to a ring position.[1] These migrations may be thermally induced, or acid[1] or base catalyzed.[2]

$$Z = N, O, C$$
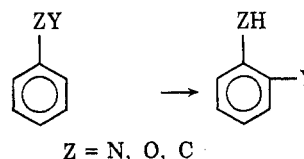
The purpose of this report is to call attention to the rather general existence of this kind of thermally induced migration which arises during the high-temperature pyrolyses of appropriately substituted aromatic compounds. The recently reported conversion of phenylacetonitrile to *o*-tolunitrile by our laboratories[3] and by Wentrup and Crow[4] is an example of such a migration (see Table I). The relatively high yield of ortho isomer relative to meta and para isomers (tolunitrile) suggests the participation of an intramolecular migration.[1] On the other hand, competitive cleavage also occurs, as shown from the formation of benzene, toluene, and the isomeric cyanophenylacetonitriles.

Many of these side chain to ring migrations are obscured because the initially formed rearrangement

(1) M. J. S. Dewar in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, Chapter 5.

(2) W. von E. Doering and R. A. Bragole, *Tetrahedron,* **22**, 385 (1966).

(3) N. F. Haidar, Ph.D. Thesis, University of Kentucky, Lexington, Ky., 1970.

(4) C. Wentrup and W. D. Crow, *Tetrahedron,* **26**, 3965 (1970).

TABLE I
RELATIVE CONCENTRATIONS[a] OF PYROLYSATE COMPONENTS OBTAINED FROM PHENYLACETONITRILE AT 850°

Compd	Concn, %
Benzene	3.1
Benzonitrile	0.6
α-Cyano-*m*-tolunitrile	0.4
α-Cyano-*o*-tolunitrile	1.1
α-Cyano-*p*-tolunitrile	1.1
Diphenylacetonitrile	0.8[b]
Fluorene	0.8[b]
Indole–cinnamonitrile	0.4
Phenanthrene–anthracene	0.1
Phenylacetonitrile	80.4
2-Phenylindole	0.2
p-Phenylphenylacetonitrile	0.3
trans-Stilbene	0.6
Toluene	7.6
o-Tolunitrile	3.0
Wt of pyrolysate, g	8.8
Wt pyrolyzed, g	10.2

[a] Relative concentrations are area per cent as determined by glpc analysis. [b] Unseparated mixture of diphenylacetonitrile and fluorene.

products undergo ring closure. Thus, the results of experiments reported in Tables II and III show that

TABLE II
RELATIVE CONCENTRATIONS[a] OF PYROLYSATE COMPONENTS OBTAINED FROM DIPHENYLMETHANE AND *o*-METHYLBIPHENYL AT 850°

Component	Substance pyrolyzed Diphenylmethane	*o*-Methylbiphenyl
Anthracene	0.5	
Benzene	9.7	6.7
Biphenyl	0.4	
Diphenylmethane	64.6	
Fluorene	7.6	45.1
Indene	0.2	
o-Methylbiphenyl		39.6
m-Methylbiphenyl	0.5	0.7
p-Methylbiphenyl	0.7[b]	1.0
Naphthalene	0.1	0.1
trans-Stilbene	1.2[c]	
Styrene	0.1	
Toluene	8.6	3.7
Triphenylmethane	0.7	
Wt of pyrolysate, g	3.80	5.70
Wt of substance pyrolyzed, g	4.02	6.16

[a] Relative concentrations are area per cent as determined by glpc analysis. [b] Fraction also contained acenaphthylene. [c] Identification based upon glpc retention time and uv spectrum.

the formation of fluorene from diphenylmethane[5] and of dibenzofuran from phenyl ether probably arises from the rearrangement products *o*-methylbiphenyl and *o*-hydroxybiphenyl, respectively. Likewise the formation of acridine from *N*-benzylaniline[6] undoubtedly involves the proposed side chain to ring migration. Carbazole formation from diphenylamine[7] and phenanthrene formation from bibenzyl[5] are further examples of the rearrangement.

(5) J. W. Sweeting and J. F. K. Wilshire, *Aust. J. Chem.*, **15**, 89 (1962).
(6) H. Meyer and A. Hofmann, *Monatsh.*, **37**, 698 (1916).
(7) C. Graebe, *Justus Liebigs Ann. Chem.*, **167**, 125 (1873).

TABLE III
RELATIVE CONCENTRATIONS[a] OF PYROLYSATE COMPONENTS OBTAINED FROM *o*-HYDROXYBIPHENYL AND PHENYL ETHER AT 700°

Component	Substance pyrolyzed *o*-Hydroxybiphenyl	Phenyl ether
A. Neutral Fraction		
Benzene	4.0	0.4
Biphenyl	4.6	
Dibenzofuran	10.7	2.0
Naphthalene	0.05	0.4
Phenyl ether		96.7
Wt of neutral fraction, g	20.1[b]	5.4
B. Acid Fraction		
o-Hydroxybiphenyl	76.3	
Phenol	4.1	94.0
Wt of acid fraction, g	20.1[b]	0.3
Wt of substance pyrolyzed, g	20.2	6.0

[a] Relative concentrations are area per cent as determined by glpc analysis. [b] Combined weight of acid and neutral fractions.

Experimental Section

Ultraviolet spectra were measured in cyclohexane using a Perkin-Elmer Model 202 spectrophotometer, infrared spectra were measured in chloroform or carbon tetrachloride using a Beckman IR-8 spectrophotometer equipped with a mirror beam condenser, and nmr spectra were measured in deuteriochloroform or carbon tetrachloride (TMS internal standard) using a Varian T-60 spectrometer. Mass spectra were determined on a Hitachi RMU-6E double focusing mass spectrometer using 70 eV ionizing energy with the inlet system at 200°. Glpc analyses and preparative separations of the pyrolysate constituents were carried out on an F & M Model 810 gas chromatograph using a thermal conductivity detector.

Materials.—The substances pyrolyzed were commercially available samples and were used as received. Purities were checked prior to use by glpc analysis.

Pyrolyses.—The pyrolyses were carried out in the apparatus previously described[8] using 20–30 ml of Berl saddles or Vycor beads, and a syringe driven by a Troemer monodrum for the introduction of liquid samples (or a rotating screw device for solid samples) into the pyrolysis tube. Addition rates were *ca.* 4.5 g/hr. Nitrogen gas flow rates were 60 ml/min in the phenylacetonitrile, diphenylmethane, and *o*-methylbiphenyl pyrolyses and 100 ml/min in the *o*-hydroxybiphenyl and phenyl ether pyrolyses. The liquid products were collected in two traps, each of which was cooled in a Dry Ice–chloroform–carbon tetrachloride mixture, and dissolved in ether. The *o*-hydroxybiphenyl pyrolysate was separated into neutral and acidic fractions by extraction with 5% NaOH.

Separation and Identification of Components.—Components of the neutral and acidic fractions were separated by glpc using a 25 ft × 0.375 in. 20% Apiezon L (Anakrom 50/60 U) column heated isothermally at 90° for 8 min and then programmed at 2°/min or 4°/min to 280°.

Identifications of components are based on comparisons of glpc retention times, ultraviolet spectra, and infrared spectra with those obtained from authentic samples with the following exceptions. The identifications of diphenylacetonitrile and *p*-phenylphenylacetonitrile were based upon comparisons of glpc retention times, infrared spectra, mass spectra, and nmr spectra with those obtained from authentic compounds. Biphenyl and dibenzofuran were identified from comparisons of glpc retention times and ultraviolet and nmr spectra. Estimation of relative abundances of constituents are based on area per cent values obtained from glpc analyses. The results are reported in the tables.

(8) J. M. Patterson, A. Tsamasfyros, and W. T. Smith, Jr., *J. Heterocycl. Chem.*, **5**, 727 (1968).

(73) with the Agricultural Research Service, U. S. Department of Agriculture, administered by the Athens, Ga. Area, Richard B. Russell Agricultural Research Center, Athens, Ga. 30604.


Steric Factors in the Solvolysis of Haloallenes

MELVYN D. SCHIAVELLI,* PATRICIA L. TIMPANARO, AND ROBERT BREWER

Department of Chemistry, College of William and Mary, Williamsburg, Virginia 23185
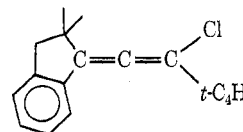
Earlier work[1-3] has established the mechanism of solvolysis of trisubstituted haloallenes in aqueous acetone and aqueous ethanol solutions as a unimolecular C–X bond heterolysis yielding the resonance-stabilized cation, 1. The solvolysis reaction of the haloallenes

1
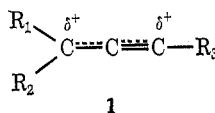
studied parallels the S$_N$1 reaction of saturated systems in every respect. First-order rate laws are obeyed, a large excess of added nucleophile has no effect on the rate of solvolysis, a common ion rate depression is observed, the substituent effects and temperature and solvent dependence of the reaction rate are consistent with a carbonium ion mechanism, and products derived from reaction at each end of 1 are observed.

It was noted, however, that an aromatic ring at C-1 had a much larger effect on the rate of solvolysis than one placed at C-3. For example, 1-chloro-1-phenyl-3-*tert*-butyl-4,4-dimethyl-1,2-pentadiene (R$_3$ = C$_6$H$_5$; R$_1$ = R$_2$ = *tert*-butyl) solvolyzes eight times as rapidly as 3-chloro-2,2,6,6-tetramethyl-5-phenyl-3,4-heptadiene (R$_1$ = R$_3$ = *tert*-butyl; R$_2$ = C$_6$H$_5$) in 50:50 (v/v) acetone–water at 35°. This is apparently due to the inability of an aromatic ring in the 3 position to achieve the coplanarity necessary for overlap with the developing electron-deficient π MO of the cation. A similar situation obtains in the solvolysis of aralkyl chlorides where 1-chloro-2,2-dimethylindane is reported to solvolyze 10^4 times as fast as 1-chloro-1-phenyl-2,2-dimethylpropane in 80% ethanol at 45°.[4,5]

To test this hypothesis in our system the allenyl halide 2 was prepared. Treatment of the propargyl alcohol obtained upon nucleophilic addition of *tert*-butylethynyllithium to 2,2-dimethylindan-1-one with

(1) M. D. Schiavelli, S. C. Hixon, and H. W. Moran, *J. Amer. Chem. Soc.*, **92**, 1082 (1970).
(2) M. D. Schiavelli, S. C. Hixon, H. W. Moran, and C. J. Boswell, *J. Amer. Chem. Soc.*, **93**, 6989 (1971).
(3) M. D. Schiavelli, R. P. Gilbert, W. A. Boynton, and C. J. Boswell, *J. Amer. Chem. Soc.*, **94**, 5061 (1972).
(4) G. Baddeley and J. Chadwick, *J. Chem. Soc.*, 368 (1951).
(5) G. Baddeley, J. W. Rasburn, and R. Rose, *J. Chem. Soc.*, 3168 (1958).

2

SOCl$_2$ afforded the desired chloroallene. The data in Table I support the conclusion that 2 reacts by a

TABLE I
RATES OF SOLVOLYSIS OF 2 IN AQUEOUS ACETONE SOLVENT

Acetone–water (v/v)	T, °C	$10^4 k$, sec^{-1}
70:30	24.62 ± 0.01	13.0 ± 0.3
80:20	24.62 ± 0.01	2.89 ± 0.03
90:10	24.62 ± 0.01	0.463 ± 0.004
90:10	34.68 ± 0.02	1.68 ± 0.03
90:10	45.30 ± 0.02	4.47 ± 0.03

mechanism identical with that of other trisubstituted haloallenes. A plot of these data *vs.* Y yields $m = 0.73$. The temperature dependence of the rate constant yields $\Delta H^{\ddagger} = 20.0$ kcal/mol and $\Delta S^{\ddagger} = -11.0$ eu at 25°. These data also point up the remarkable rate enhancement over the structurally similar compound 3 (R$_1$ = R$_3$ = *tert*-butyl; R$_2$ = C$_6$H$_5$). The
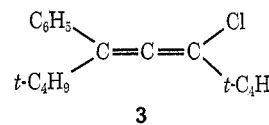
3

indanyl derivative, 2, reacts 6800 times as fast as the open-chain analog, 3, in 90:10 acetone–water at 35°.

It is likely that some of this rate acceleration is due to the presence of an ortho alkyl substituent in the fused-ring compound which is not present in the open-chain compound. However, for this rate acceleration to be accounted for solely by the substituent effect, ρ must equal −12, a value at least twice as large as that observed for any other solvolysis reaction. Furthermore, since no hybridization changes occur at C-3, any strain introduced by the five-membered ring remains the same in the ground state and transition state. Thus, no change in rate due to the introduction of strain in the ground state is to be expected. It seems likely therefore that a major portion of the rate enhancement is associated with the constrained coplanarity of the aromatic ring and vacant π MO and the attendant stabilization of 1. We have attempted unsuccessfully thus far to prepare analogs of 2 and 3 having substituents in the aromatic ring in an attempt to assess the magnitude of substituent effects on this system.

Experimental Section

All melting points and boiling points are uncorrected. Ir spectra were obtained using a Perkin-Elmer Model 457 spectrophotometer or a Bausch and Lomb Model 250 spectrophotometer. Nmr spectra were obtained using a Perkin-Elmer Model R-20B spectrometer. Microanalyses were performed by Atlantic Microlabs, Atlanta, Ga.

2,2-Dimethyl-1-indanone was prepared by dialkylation of 1-indanone with methyl iodide and potassium *tert*-butoxide in *tert*-butyl alcohol according to Woodward, *et al.*[6] Distillation at reduced pressure (80–81° at 0.7 mm) afforded the ketone in

(6) R. B. Woodward, A. A. Patchett, D. H. R. Barton, D. A. J. Ives, and R. B. Kelly, *J. Chem. Soc.*, 1131 (1957).