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Phenyl Shifts in Substituted Arenes via *Ipso* Arenium Ions

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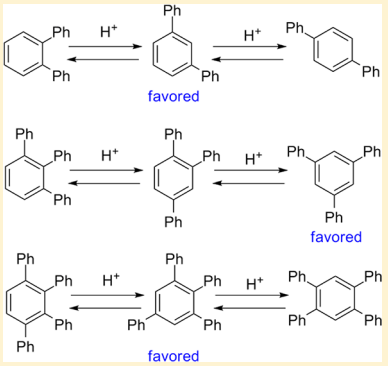
Supporting Information

ABSTRACT: The isomerization of substituted arenes through *ipso* arenium ions is an important and general molecular rearrangement that leads to interconversions of constitutional isomers. We show here that the superacid trifluoromethanesulfonic acid (TfOH), ca. 1 M in dichloroethane (DCE), provides reliable catalytic reaction conditions for these rearrangements, easily applied at ambient temperature, reflux (84 °C), or in a microwave reactor for higher temperatures. Interconversion of terphenyl isomers in TfOH/DCE at 84 °C gives an *ortho*/*meta*/*para* equilibrium ratio of 0:65:35, nearly identical to values reported earlier by Olah with catalysis by $AlCl_3$. For the three triphenylbenzenes, TfOH-catalyzed equilibration strongly (>95%) favors the 1,3,5-triphenyl isomer. Equilibration of the three possible tetraphenylbenzenes gives a 61:39 mixture of the 1,2,3,5- and 1,2,4,5-substituted isomers. Under the reaction conditions explored, none of these structures undergoes significant Scholl cyclization. DFT calculations with inclusion of solvation support a mechanistic scheme in which all of the phenyl migrations occur among a series of *ipso* arenium ions. In every case studied, the preferred isomers at equilibrium are those that yield highly stable cations by the most exothermic, hence least reversible 1,2-H shift.

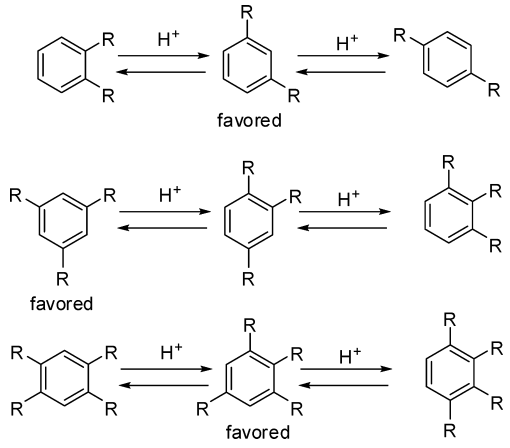


INTRODUCTION

Soon after discovery of the Friedel–Crafts alkylation in 1877,[1] it was noted that in some unusual cases, *meta*-disubstituted products can be formed, instead of the usual *ortho* + *para* product mixture.[2−4] Early suggestions that this result may be due to secondary isomerization were supported by Baddeley's report in 1935 that *p*-dipropylbenzene rearranges to the *meta* isomer upon heating in the presence of $AlCl_3$.[5] Over the next two decades, investigations by Baddeley,[6] Nightingale,[1b,7] Norris,[8] Allen,[9] McCaulay,[10] Brown,[11] and others established the generality of acid-catalyzed alkyl group migrations in substituted benzenes under Friedel–Crafts reaction conditions. In these reactions, $AlCl_3$ or $AlBr_3$ usually are assumed to generate a protic acid through reaction with of adventitious water.[12] It is commonly observed that disubstituted alkylbenzenes favor the *meta* isomer at equilibrium (Scheme 1), trisubstituted benzenes favor products with 1,3,5-substitution patterns, and tetrasubstituted structures favor products with 1,2,3,5-substitution. Baddeley suggested a carbocation mechanism,[6] which was soon supported by Nightingale's reports of simultaneous side-chain isomerization of *sec*-butyl to *tert*-butyl.[7a] McCaulay presented the first clear description of a mechanism passing through *ipso* arenium ions.[10] Key mechanistic details of these rearrangements were next laid out in a series of papers by Olah and co-workers, who ascribed the common preference for *meta*-substitution in alkylbenzenes to formation of the most stable cation and also described similar isomerizations of halobenzenes.[13] This general type of rearrangement has been referred to as a "Baddeley isomerization"[14] or a "Friedel–Crafts isomerization".[13]

Scheme 2 presents the essential mechanism for rearrangements in a disubstituted benzene. Among the nine possible

Scheme 1. Acid-Catalyzed Interconversions of Substituted Benzenes (R = Alkyl)



carbocations (also known as σ complexes[15]) that are interconvertible by 1,2-shifts, substituent migration can only occur through the "*ipso*" arenium ions shown, in which a substituent and hydrogen share a carbon atom. The lowest energy cations on this surface are accessible by 1,2-H shifts in the *meta* isomer; this clearly plays a major role in determining the favored product.

Gas-phase electrophilic substitution reactions of alkylbenzenes show some parallel behavior but may involve both σ and π complexes; this is a subject of some current debate.[16]

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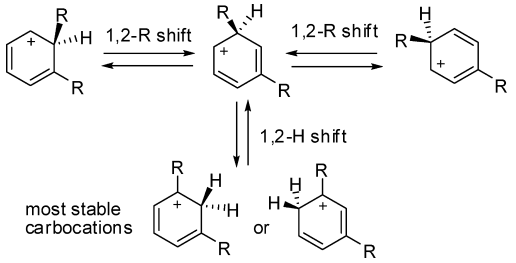
Scheme 2. Carbocation Interconversions in Disubstituted Benzenes



Substituent scrambling within arenes in mass spectrometry is well-known and has been reviewed by Kuck.[17] The existence of *ipso* arenium ions has been amply demonstrated through their trapping in electrophilic nitration reactions.[18] Alkyl group transfer (transalkylation) from *ipso* arenium ions is also well-known.[19]

Much is known about the ability of phenyl groups to migrate in pinacol and other rearrangements.[20] It is surprising that phenyl migration in arenium ions has not been as well investigated. Acid-catalyzed interconversion of terphenyl isomers was first described by Allen and Pingert in 1939.[21] These authors reported that *o*-terphenyl (**1**) is first converted to *meta* (**2**) by heating with $AlCl_3$, with slower conversion to the *para* isomer **3**, which was believed to be the eventual product. Two decades later, with analysis by infrared spectroscopy, Olah and Meyer reported a 0:63:37 *ortho*/*meta*/*para* equilibrium product ratio upon heating any of the three isomers with $AlCl_3$ in sealed tubes.[13a] In one especially revealing experiment reported in 1963, Wynberg used a ^{14}C-labeled substrate to demonstrate complete carbon atom scrambling by phenyl migration in biphenyl.[22] Scott and co-workers later showed that this process occurs through stepwise phenyl migrations on the opposing ring. An initial *ipso* carbon label migrates successively to *ortho*, *meta*, and then *para* positions.[23] Tolbert and co-workers studied triflic acid catalyzed rearrangements in dimethylbiphenyls, noting a high preference for di-*meta* substitution at equilibrium, which was their synthetic objective.[24] In this case, it is not possible to distinguish between phenyl or methyl migrations as the source of rearrangement. More complex examples of reactions that proceed through *ipso* arenium ions include automerization of 1,2,3,4-tetrahydrophenanthrene[25] and phenanthrene,[26] both demonstrated through ^{13}C labeling studies. Balaban's report of an acid-catalyzed automerization of naphthalene was later shown to be in error,[27] but this reaction seems likely to occur at higher temperature. Examples of unexpected phenyl migrations under conditions of acid catalysis or Scholl reaction are scattered in the literature.[28]

There have been few theoretical studies on this type of arenium ion rearrangement. Tolbert and co-workers used AM1 methods to study dimethylbiphenyls, showing high correspondence between equilibrium product ratios and the relative free energies of carbocations.[24] Several groups have employed Hartree–Fock methods to study related π complexes.[16e,g,29] Motivated by results from gas phase and mass spectrometric studies,[17] Kolboe recently used DFT methods in a thorough study of the complex interconversions among monoalkylbenzenes and xylenes, including higher energy ring-expansion reactions[30] and a computational search for π complexes.[16b−d]

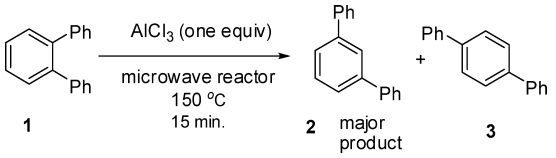
Another early discovery in arenium ion chemistry was the Scholl reaction[31] in which arenes either oligomerize or cyclize upon treatment with $AlCl_3$ or protic acids.[32] Variations on the Scholl reaction have been widely applied in the synthesis of polycyclic aromatic compounds,[33] but the reaction mechanism has remained somewhat mysterious and may be closely linked to arenium ion rearrangements.[34] As noted above, rearrangement by phenyl migration can be a major impediment to synthesis.[28b]

RESULTS AND DISCUSSION

Previous work in this field has demonstrated a general and synthetically useful reaction in which substituted arenes interconvert through acid catalysis, with the intermediacy of *ipso* arenium ions. As our first effort in a more systematic study, we report here experimental and computational results on phenyl migrations by the *ipso* arenium ion mechanism.

Initial Experiments. Our entry into this field was serendipitous. We recently described the technique of microwave flash pyrolysis (MFP) in which high-temperature pyrolytic conditions are approached by heating mixtures of organic substances with graphite or carbon nanotubes in a microwave reactor.[35] MFP reaction of *o*-terphenyl (**1**) on graphite gave only a 10% yield of triphenylene, the major product being naphthalene. Since the desired cyclization is essentially an intramolecular Scholl reaction, we next explored anhydrous $AlCl_3$ as the solid phase. Heating mixtures of **1** with $AlCl_3$ in a microwave reactor (Scheme 3) led to *m*-terphenyl

Scheme 3. Microwave Rearrangement of *o*-Terphenyl



(**2**) as the major product, with a small amount of the *para* isomer (**3**). We quickly learned that the $AlCl_3$-catalyzed interconversion of terphenyl isomers was reported by Allen and Pingert in 1942[21] and shown by Olah and Meyer in 1962 to give primarily the *meta* isomer.[13a]

Reaction Conditions: Moving Beyond AlX_3 Catalysis. These isomerizations are usually assumed to occur by protic acid catalysis, with the acid generated from reaction of adventitious traces of water with $AlCl_3$ or $AlBr_3$. This can generate HX (X = Cl or Br), but it seems more likely that the acid is an AlX_3–H_2O or AlX_3–HX complex, which is probably a stronger acid. Previous reports[24,36] and our own experimentation with other protic acids led use to choose trifluoromethanesulfonic acid (**4**, TfOH) in 1,2-dichloroethane (DCE) as a more reliable alternative to $AlCl_3$. The absolute pK_a of TfOH in DCE is not known, but it is considered to be a superacid[37] in this solvent, with a pK_a of −11.4, vs picric acid as zero.[38] DCE is a non-nucleophilic thermally stable solvent that is sufficiently polar to support cationic intermediates.[39] We find that TfOH-catalyzed reactions in DCE proceed most conveniently at reflux (84 °C) but can also be run to at least 160 °C in a microwave reactor. Optimal conditions proved to be 1.1 M TfOH in DCE (ca. 1:5 v/v).

It is noteworthy that dissolution of any of the arenes studied in TfOH/DCE immediately yields brightly colored solutions, with each arene displaying a unique color. This color persists

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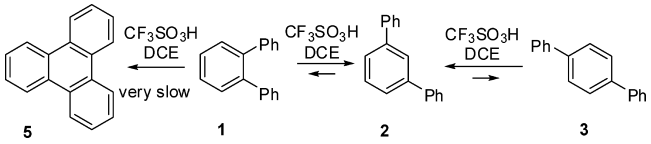
until the reaction is neutralized and may be due to low equilibrium concentrations of the cations. Protonated arenes are known to absorb in the visible region.[40]

Equilibrium Ratios and Relative Rates in Rearrangements of Terphenyl Isomers. Our initial experiments using either $AlCl_3$ or TfOH as catalyst led to equilibrium mixtures in which the *meta* isomer is heavily dominant. Although this result is in agreement with earlier studies, it seemed essential to establish the product ratios at prolonged reaction. Pure samples of each terphenyl isomer (ca. 10^{-2} M) were refluxed (Scheme 4) with 1.1 M TfOH in DCE, with products monitored by

Scheme 4. Interconversions of Terphenyl Isomers



capillary GC analysis of neutralized aliquots. Under these conditions, *ortho* isomer **1** reacts very rapidly. After 1 h at reflux, the mixture was 97% *meta* isomer, followed by slower formation of a *meta*/*para* mixture that equilibrated at 65:35, consistent with Olah's observation.[13a] Only <0.1% of the *ortho* isomer was present at equilibrium. The *para* isomer **3** rearranged more slowly, again giving mostly meta and with a slow evolution toward a 65:35 ratio. *m*-Terphenyl (**2**) rearranged most slowly to give essentially the same equilibrium ratio. The same product ratio was obtained starting with a 50:50 *meta*/*para* mixture. In every case, only a trace (<1%) of *ortho* isomer is present at equilibrium. At prolonged reaction times, minor byproducts, primarily biphenyl and triphenylene (**5**), appeared in the chromatograms, but analysis of the final products by ^{1}H NMR showed almost exclusively terphenyls. These conditions clearly do not favor Scholl cyclization of **1**. We did not see evidence for any significant quantities of oligomers from **1**, which were previously seen by King under Scholl conditions ($MoCl_5/CH_2Cl_2$).[34b] Not surprisingly, heating triphenylene in TfOH/DCE under the same conditions did not cause reversion to **1** or its isomers.

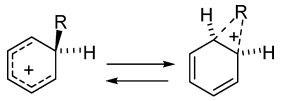
Carrying out the same reactions in a microwave reactor allowed for higher temperatures and more rapid approach to equilibrium. As one example, heating **1** at 140 °C in TFOH/DCE for one hour gave a mixture that was <0.1% *ortho*/69% *meta*/31% *para*. Longer reaction times or higher temperatures did not significantly change this result.

Our results for terphenyl are thus in good agreement with Olah's earlier observation[13a] and clearly demonstrate protic acid catalysis. An initial product distribution that heavily favors the *meta* isomer may be preparatively useful if monitored closely. This very slowly (1−3 days) evolves to a *meta* + *para* mixture that is consistently ca. 65:35. Only traces of triphenylene are formed by Scholl cyclization.

Computational Models for Terphenyl Rearrangements. The energetics of protonation and the potential surface for rearrangements were investigated with density functional theory using Spartan 10,[41] Gaussian 03, or Gaussian 09.[42] All calculations reported here are at the B3LYP/6-31+G(d,p) level of theory. This density functional has been widely used to study carbocation chemistry.[43] The polarizable continuum model (PCM) was employed to assess solvation in dichloroethane.[44]

As with most carbocations, arenium ions undergo facile rearrangements. Table 1 summarizes free energy barriers to

Table 1. B3LYP/6-31+G(d,p) Free Energy Barriers to Rearrangement (kcal/mol) at 298 K



6 TS7

substituent (R)	$\Delta G^{\ddagger}$	$\Delta G^{\ddagger}$ (DCE solvated)
R = H	11.46	10.75
R = CH_3	18.44	17.88
R = Ph	9.73	12.57
R = Br	6.67	8.01

degenerate rearrangements in benzenium ions for hydrogen and other common migrating groups. The transition-state structure for phenyl migration is shown in Figure 1. The effect

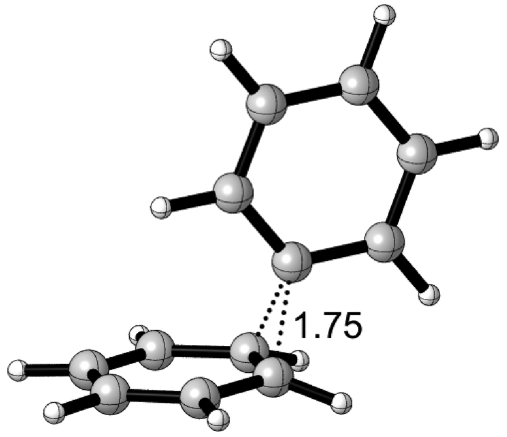


Figure 1. B3LYP/6-31+G(d,p) transition state structure (**TS7**, R = Ph) for phenyl migration.

of solvation on barriers to rearrangement is seen to be quite modest. For R = H, Olah used NMR line shape analysis to measure a barrier of 10 ± 1 kcal/mol in superacid media.[45] Radom and co-workers calculated a barrier of 8.2 kcal/mol based on G2(MP2) theory.[46]

One critical question is the energetics of protonation. Scheme 5 summarizes the free energies calculated for proton transfer from TfOH (**4**) to form the lowest energy cation of *m*-terphenyl in silico and using a PCM model in 1,2-dichloroethane. The predicted change in solvation energies in this modestly polar solvent (dielectric constant = 10.3) is surprisingly large at 75.8 kcal/mol. If any doubt remained, these results provide clear support for a carbocation mechanism.

Figure 2 summarizes the free energies of relevant stationary points on this energy surface, with inclusion of DCE solvation. The combined energies of cation **1b** + triflate anion have been chosen as a reference point, thus both the protonation steps and rearrangements share an energy scale. The top portion of this figure represents interconversions among the *ipso* cations **1b**, **2b**, and **3b**, which have modest barriers for phenyl migration. We have not calculated the barriers, but 1,2-H shifts should easily convert these with the lower energy non-*ipso* cations **1a**, **2a**, and **3a**.

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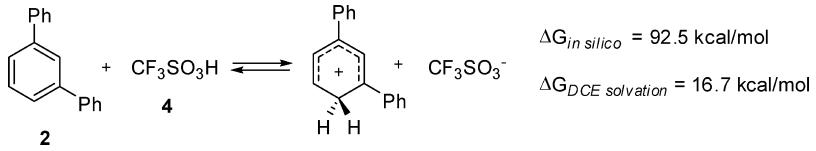
Scheme 5. Energetics of Protonation by Triflic Acid (4)



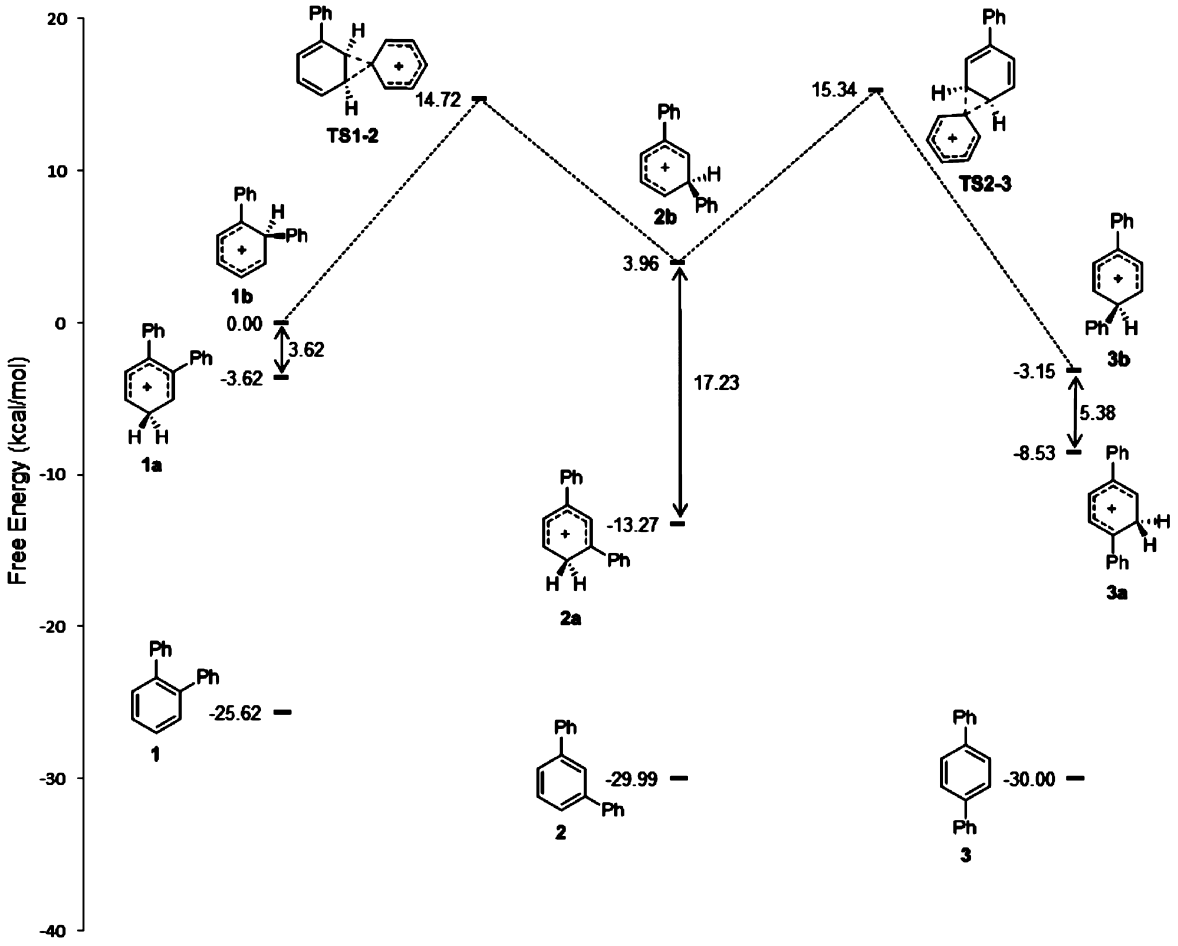
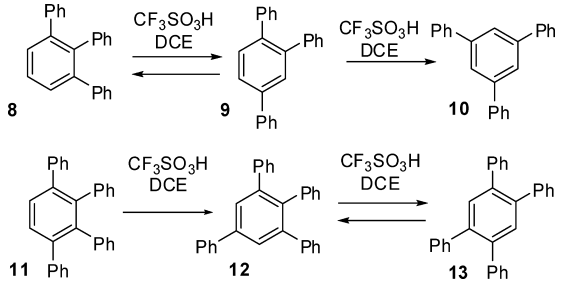


Figure 2. Energetics of protonation and rearrangements in terphenyl isomers.

In principle, true thermodynamic equilibration would reflect the relative energies of neutral isomers and give a ca. 1:1 mixture of *meta* and *para* isomers. It seems likely that this stage is never reached. Interconversion of isomers requires an initial pre-equilibrium which generates the *ipso* arenium ion, probably through 1,2-H shift from a lower energy isomer. Phenyl migrations are followed by direct deprotonation or 1,2-H shifts to the lower energy cation, followed by deprotonation. A detailed kinetic model would require a large assembly of equilibrium and rate constants; however, results in hand allow some important conclusions about relative rates of reaction and the equilibrium product. After protonation of **1** to give its lowest energy cation **1a**, the net barrier to rearrangement is 18.34 kcal/mol (3.62 for 1,2-H shift +14.72 for rearrangement), consistent with the observed rapid reaction at 84 °C. For **3**, which rearranges more slowly, the barrier is 23.87 kcal/mol (8.53 + 15.34). The *meta* isomer **2** is easiest to protonate but slowest to react because it has the highest barriers to rearrangement; 28.0 and 28.6 kcal/mol by the same two step path. In the equilibration of cationic species, the dominance of **2a** and hence neutral product **2** is determined not just by its low energy but the highly exothermic rearrangement of **2b** to **2a** by 1,2-H shift.

Rearrangements of Tri- and Tetraphenylbenzenes. Scheme 6 summarizes our experimental results for the isomeric tri- and tetraphenylbenzenes. In each case, rearrangement was carried out with pure isomers in refluxing TfOH/DCE or at higher temperatures in a microwave reactor. Product mixtures

Scheme 6. Rearrangement of Tri- and Tetraphenylbenzenes



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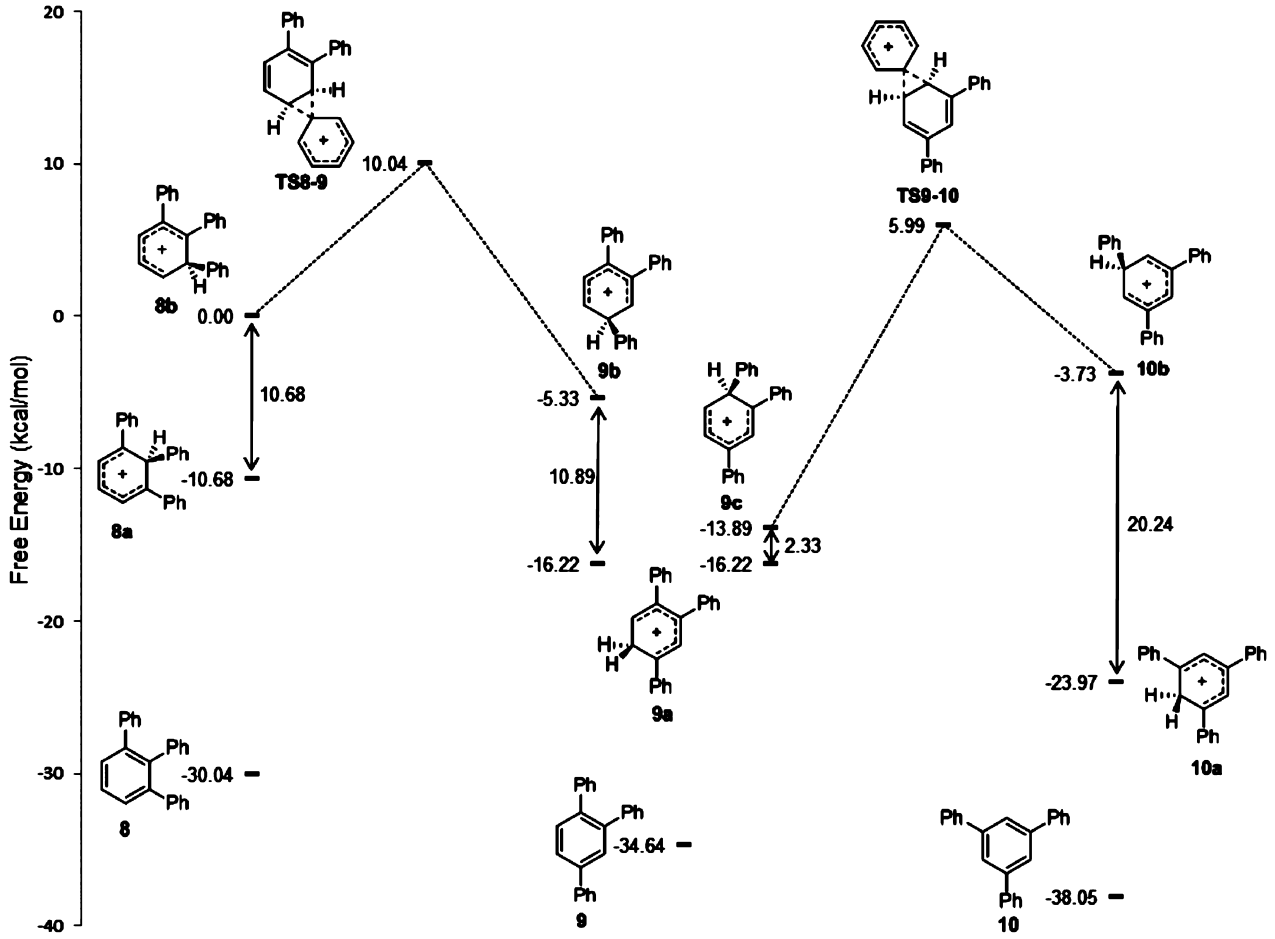

Figure 3. Energetics of protonation and rearrangements in triphenylbenzenes.

were analyzed by 400 MHz ^{1}H NMR spectroscopy since each isomer is easily identified by characteristic resonances.[47]

In the triphenylbenzene series, the 1,2,3-isomer (**8**) rearranged quickly (15 min) to isomer **9** which then rearranged more slowly to **10**. Not surprisingly, **10** proved to be nearly inert in these reactions, generating only ca. 8% of the 1,2,4-isomer at the highest temperature explored. We note that 1,3,5-triarylbenzenes are often synthesized by the acid catalyzed aldol condensation of acetophenones.[48] An unrecognized key to success in this chemistry is likely to be the absence of rearrangement for 1,3,5-trisubstituted benzenes!

Tetraphenylbenzenes underwent somewhat slower reaction. The 1,2,3,4-tetraphenyl isomer (**11**) rearranged in refluxing TfOH/DCE to a 61:39 mixture of **12** and **13**. These isomers were separated by chromatography for characterization. A similar product distribution was reached in a microwave reactor at 130 °C, beginning with either pure **11** or **13**.

Figures 3 and 4 present summaries of free energies (with solvation in DCE) for relevant cations and transition states in the tri- and tetraphenylbenzene series. As above, the chosen reference point is a rearranging cation plus triflate anion, thus both protonation and rearrangement are represented in these diagrams. For the triphenyl isomers, energetics of cationic species are consistent with the sequential isomerization **8** to **9** to **10**. Rearrangement of protonated **8** proceeds through a barrier of 20.72 kcal/mol (10.68 + 10.04); this is both rapid and unidirectional toward **9**. For protonated **9**, the lower barrier (22.2 vs 26.3) proceeds toward **10**. This protonated structure is in the deepest energy well (23.97 + 5.99 kcal/mol) and gives rearrangement product only under extreme conditions. Once again, the equilibrium product is determined by the cation which is not only most stable but has the most exothermic 1,2-H shift (**10b** to **10a**).

In the tetraphenylbenzene isomers, catalyzed equilibration proceeds somewhat more slowly to a mixture of two products (Scheme 6). According to Figure 4, the tetraphenyl isomers should be most easily protonated but also show some of the highest barriers to rearrangement; both effects are due to enhanced resonance stabilization. Protonation of the center ring of **11** directly yields the *ipso* cation needed for rearrangement, thus **11** rearranges easily to **12**. Cations **12b**, **12c**, and **13b** have similarly exothermic rearrangements to stable isomers; this explains why their neutral counterparts **12** and **13** dominate at equilibrium.

■ CONCLUSIONS

The isomerization of substituted arenes through *ipso* arenium ions is an important and general molecular rearrangement that can lead to interconversions of ring substituents, as well as more complex processes. This reaction has been known empirically since the late 19th century from studies on Friedel–Crafts reactions.[2−4] Baddely and Kenner described the first example of a *para* to *meta* rearrangement in 1935, thus explaining the origin of unusual products in Friedel–Crafts alkylations.[5] This was followed by a series of papers by many authors which demonstrated the generality of substituent

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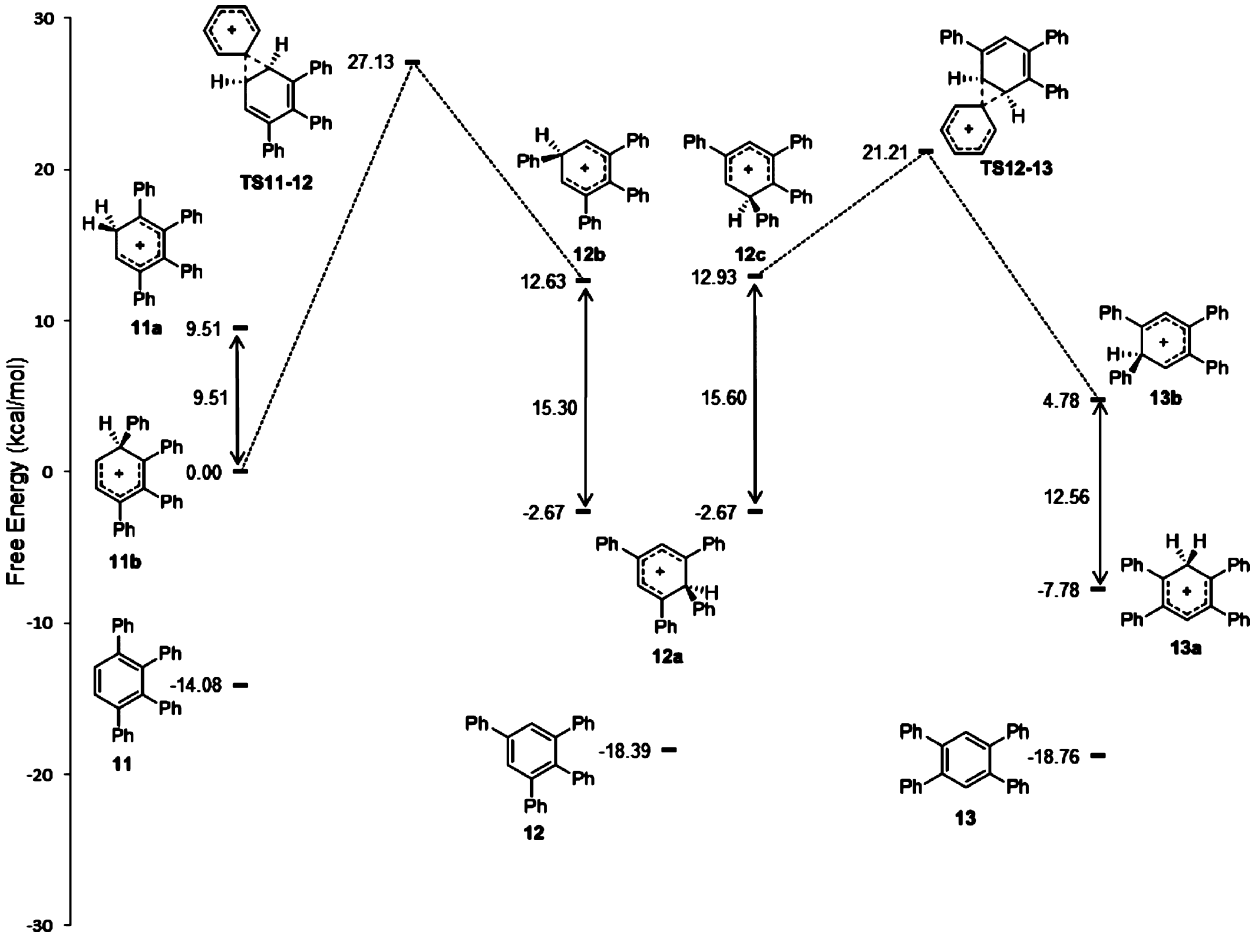

Figure 4. Energetics of protonation and rearrangements in tetraphenylbenzenes.

rearrangement in alkylbenzenes.[6−11] Olah explained the general preference for *meta*-disubstituted products through the intermediacy of *ipso* arenium ions, which lead through 1,2-H shifts to the most stable carbocation.[13] The majority of this earlier work was carried out under Friedel−Crafts conditions using aluminum trihalides as catalysts. This process has often been referred to as the Baddeley or Friedel−Crafts rearrangement.

We have shown here that the superacid trifluoromethanesulfonic acid (TfOH) in dichloroethane[38] provides more reliable catalytic reaction conditions, easily applied at ambient temperature, reflux or in a microwave reactor for higher temperatures. Rearrangements of terphenyl isomers have been reported earlier;[13a,21] our experiments confirm a preference for *meta* terphenyl at equilibrium, giving *ortho*/*meta*/*para* equilibrium ratios of 0:65:35, nearly identical to values reported earlier by Olah. For triphenylbenzenes, acid catalyzed equilibration strongly favors the 1,3,5-triphenyl isomer. Equilibration among the three possible tetraphenylbenzenes reproducibly gives a 60:40 mixture of the 1,2,3,5- and 1,2,4,5-substituted isomers. Under the reaction conditions we explored, none of these structures undergoes significant Scholl cyclization.[32] Not surprisingly, equilibrium product ratios with phenyl substitution are similar to those described earlier for alkyl-substituted benzenes (Scheme 1).

DFT calculations support a mechanistic scheme in which all of the phenyl migrations occur among a series of *ipso* arenium ions. Computational models with inclusion of implicit solvation show barriers to phenyl migration that range from 10 to 27 kcal/mol and a wide range of stability among mechanistically related non-*ipso* cations. In every case studied here, the preferred isomers at equilibrium are those which yield highly stable cations by the most exothermic, hence least reversible 1,2-H shifts.

One great mystery is why the fundamental molecular rearrangements shown in Scheme 1 are essentially absent from chemistry textbooks and are so little known among chemists today. By contrast, the mechanistically related Scholl cyclization is much better known.[31,33c−h,34] Arenium ion rearrangements have much unrealized potential in the synthesis of polycyclic aromatic structures and should be suspected whenever substituted arenes are subjected to Friedel−Crafts or Scholl reaction conditions.

■ EXPERIMENTAL SECTION

General Methods. Trifluoromethanesulfonic acid (TfOH, 99% purity) and dichloroethane (DCE, 99+%) were used as received from commercial sources. Glassware was oven-dried, and all reactions were run under a nitrogen atmosphere. ^{1}H NMR spectra were measured in $CDCl_3$ at 400 MHz and reported relative to TMS. Capillary analytical gas chromatography was performed using a DB-3 column (30 m × 0.320 mm), with temperature programming from 75 to 250 °C. For terphenyl isomers, retention times were as follows: **1**, 14.7 min; **2**, 17.9 min; **3**, 18.7 min; **5**, 25.5 min. Microwave reactions were conducted using a CEM Discover single-mode microwave reactor in 10 mL vessels with temperatures measured by an infrared sensor at the bottom of the tube. Terphenyl isomers and 1,3,5-triphenylbenzene (**10**) were commercial samples. The syntheses and NMR spectral data

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for 1,2,3-triphenylbenzene (**8**),[47b] 1,2,4-triphenylbenzene (**9**),[47a] and 1,2,3,4-tetraphenylbenzene(**11**)[47a] have been reported previously.

General Procedure for Rearrangement under Reflux. A 25 mL, two-neck round-bottom flask was equipped with a stir bar, water-cooled condenser, and glass stopper. Under a nitrogen atmosphere, the substrate (ca. 0.10 g) and 1,2-dichloroethane (DCE) (4 mL) were charged to the flask. Trifluoromethanesulfonic acid (TfOH) (0.40 mL, 4.5 mmol) was added dropwise by syringe; this typically caused formation of a bright color. The mixture was brought to reflux and monitored periodically by removal and analysis (^{1}H NMR or capillary GC) of small aliquots. Products were isolated by careful neutralization with satd aqueous $NaHCO_3$ and extraction with diethyl ether unless otherwise noted.

*Rearrangement of Terphenyl Isomers. Ortho (**1**).* By GC analysis of neutralized aliquots, *o*-terphenyl isomerized rapidly (ca. 15 min) to the *meta* isomer with slower appearance of *p*-terphenyl (see Figure S5 in the Supporting Information). After 5 days, the observed product distribution was *o*- <1%, *m*- 63%, and *p*-terphenyl 37%. An orange solid was recovered after 14 days (67%) and found to contain *o*- <1%, *m*- 66%, and *p*-terphenyl 34% by ^{1}H NMR analysis.

*Meta (**2**).* By GC analysis, slow formation of *p*-terphenyl was observed. After 5 days, the observed product distribution was *o*- <1%, *m*- 73%, and *p*-terphenyl 27%. An orange solid was recovered after 14 days (56%) and found to contain *o*- <1%, *m*- 69%, and *p*-terphenyl 31% by ^{1}H NMR analysis.

*Para (**3**).* By GC analysis, *p*-terphenyl isomerized quickly to the *m*-isomer. After 5 days, the observed product distribution was *o*- <1%, *m*- 63%, and *p*-terphenyl 37%. An orange solid was recovered after 14 days (59%) and was found to contain *o*- <1%, *m*- 62%, and *p*-terphenyl 38% by ^{1}H NMR analysis.

Rearrangement of o-Terphenyl via Microwave. *o*-Terphenyl (**1**) (0.030 g, 0.13 mmol), DCE (2 mL), and TfOH (0.2 mL, 2.2 mmol) was mixed in a 10 mL reaction tube. The reaction vessel was capped and placed in a microwave reactor (140 °C, 90 min). After the reaction time, the dark orange in solution was neutralized with satd $NaHCO_3$ and extracted using diethyl ether. An orange solid was recovered (72%) and was found to contain *o*- <1%, *m*- 64%, and *p*-terphenyl 32% and triphenylene 3% by capillary GC analysis.

Rearrangement of Triphenylbenzene Isomers. 1,2,3-Triphenylbenzene[47b] (**8**) (0.080 g, 0.26 mmol), DCE (4 mL), and TfOH (0.4 mL, 4.5 mmol) were heated to reflux, becoming red in color. Aliquots (0.5 mL) were removed periodically and neutralized. ^{1}H NMR analysis indicated that **8** isomerized rapidly to **9** (δ m 7.25−7.17 ppm, 10 H) and **10** (δ s 7.79 ppm, 3 H). After 15 min, the observed product distribution was ca. 1:1 **9**:**10**, with no starting material present. After 4.5 h, the observed product distribution was ca. 1:13 **9**:**10**.

1,2,4-Triphenylbenzene (**9**) was reacted as above, with periodic analysis of aliquots. ^{1}H NMR indicated that **9** (δ m 7.25−7.17 ppm, 10 H) isomerized quickly to **10** (δ s 7.79 ppm, 3 H), with no **8** present. After 30 min, the observed product distribution was ca. 1:5 **9**:**10**. After 4 h, the observed product distribution was ca. 1:19 **9**:**10.**

1,3,5-Triphenylbenzene (**10**) was reacted as above, with periodic analysis of aliquots. After 5 days at reflux, the reaction mixture was cooled to room temperature, neutralized, and extracted using dichloromethane. ^{1}H NMR analysis indicated only 1,3,5-triphenylbenzene, with no 1,2,3- or 1,2,4-triphenylbenzene present.

Rearrangement of 1,3,5-Triphenylbenzene via Microwave. 1,3,5-Triphenylbenzene (**10**) (0.02 g, 0.07 mmol), DCE (4 mL), and TfOH (0.40 mL, 4.5 mmol) were mixed in a 10 mL reaction tube. The reaction vessel was capped and placed in a microwave reactor (140 °C, 30 min). After cooling, the dark red mixture was neutralized with satd $NaHCO_3$ and extracted using diethyl ether. A red solid was recovered (97%). ^{1}H NMR analysis indicated the presence of **9** (δ m 7.25−7.17 ppm, 10 H) and **10** (δ s 7.79 ppm, 3 H). The product distribution was 1:11 **9**:**10**.

*Rearrangement of Tetraphenylbenzene Isomers. 1,2,3,4-Tetraphenylbenzene (**11**).* A solution of **11** (0.100 g, 2.98 mmol) in DCE (10 mL) and TfOH (1 mL, 11 mmol) was heated to reflux under nitrogen, becoming red in color. After 5 days, the reaction mixture was cooled, neutralized, extracted with dichloromethane, and concentrated in vacuo. The residue was initially purified by column chromatography over silica gel, eluting with 10% dichloromethane in hexanes giving a mixture of **12** and **13** in a 61:39 ratio and an overall yield of 96%. This isomeric mixture was separated by preparative TLC using 3% dichloromethane in cyclohexane to isolate pure **12** and **13**. A similar reaction of **11** in a microwave reactor at 130 °C for 60 min gave a mixture of **12** and **13** in a ratio of 60:40.

*1,2,4,5-Tetraphenylbenzene (**13**).* A solution of **13** (0.010 g, 0.030 mmol), DCE (2 mL), and TfOH (0.20 mL, 2.3 mmol) was subjected to microwave reaction at 150 °C for 30 min. After cooling, the dark red mixture was neutralized with satd $NaHCO_3$ and extracted using dichloromethane. A red solid was recovered (96%). ^{1}H NMR analysis indicated a product ratio of 64:36 **12**:**13**.

■ ASSOCIATED CONTENT

Supporting Information

Summary table of total energies and Cartesian coordinates for stationary points. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

This paper is dedicated to the memory of Dr. Atena Necula, a pioneer in this field.

■ REFERENCES

(1) (a) Friedel, C.; Crafts, J. M. *J. Chem. Soc.* **1877**, *32*, 725−791. (b) Nightingale, D. V. *Chem. Rev.* **1939**, *25*, 329−376.
(2) Moyle, C. L.; Smith, L. I. *J. Org. Chem.* **1937**, *2*, 112−37.
(3) Anschutz, R. *Annalen* **1886**, *235*, 150−229, 299−341.
(4) Shoesmith, J. B.; McGechen, J. F. *J. Chem. Soc.* **1930**, 2231−6.
(5) Baddeley, G.; Kenner, J. *J. Chem. Soc.* **1935**, 303−9.
(6) Baddeley, G. *J. Chem. Soc.* **1950**, 994−997.
(7) (a) Nightingale, D.; Smith, L. I. *J. Am. Chem. Soc.* **1939**, *61*, 101−104. (b) Nightingale, D.; Carton, B. *J. Am. Chem. Soc.* **1940**, *62*, 280−283. (c) Nightingale, D.; Wadsworth, F. *J. Am. Chem. Soc.* **1941**, *63*, 3514−3517.
(8) (a) Norris, J. F.; Rubinstein, D. *J. Am. Chem. Soc.* **1939**, *61*, 1163−70. (b) Norris, J. F.; Turner, H. S. *J. Am. Chem. Soc.* **1939**, *61*, 2128−2131. (c) Norris, J. F.; Vaala, G. T. *J. Am. Chem. Soc.* **1939**, *61*, 2131−4.
(9) (a) Allen, R. H.; Alfrey, T., Jr.; Yats, L. D. *J. Am. Chem. Soc.* **1959**, *81*, 42−6. (b) Allen, R. H.; Yats, L. D. *J. Am. Chem. Soc.* **1959**, *81*, 5289−92. (c) Allen, R. H. *J. Am. Chem. Soc.* **1960**, *82*, 4856−8. (d) Allen, R. H.; Yats, L. D.; Erley, D. S. *J. Am. Chem. Soc.* **1960**, *82*, 4853−6.
(10) McCaulay, D. A.; Lien, A. P. *J. Am. Chem. Soc.* **1952**, *74*, 6246−50.
(11) Brown, H. C.; Jungk, H. *J. Am. Chem. Soc.* **1955**, *77*, 5579−5584.
(12) Kramer, G. M.; Skomoroski, R. M.; Hinlicky, J. A. *J. Org. Chem.* **1963**, *28*, 2085−6.
(13) (a) Olah, G. A.; Meyer, M. W. *J. Org. Chem.* **1962**, *27*, 3682−3. (b) Olah, G. A.; Meyer, M. W. *J. Org. Chem.* **1962**, *27*, 3464−9. (c) Olah, G. A.; Tolgyesi, W. S.; Dear, R. E. A. *J. Org. Chem.* **1962**, *27*, 3455−64. (d) Olah, G. A.; Tolgyesi, W. S.; Dear, R. E. A. *J. Org. Chem.* **1962**, *27*, 3449−55. (e) Olah, G. A.; Tolgyesi, W. S.; Dear, R. E. A. *J. Org. Chem.* **1962**, *27*, 3441−9. (f) Olah, G. A.; Meyer, M. W. *J. Org.*

Chem. **1963**, *28*, 1912−14. (g) Olah, G. A.; Carlson, C. G.; Lapierre, J. C. *J. Org. Chem.* **1964**, *29*, 2687−9. (h) Olah, G. A.; Meyer, M. W.; Overchuk, N. A. *J. Org. Chem.* **1964**, *29*, 2313−15. (i) Olah, G. A.; Meyer, M. W.; Overchuk, N. A. *J. Org. Chem.* **1964**, *29*, 2315−16. (j) Olah, G. A.; Meyer, M. W.; Overchuk, N. A. *J. Org. Chem.* **1964**, *29*, 2310−12. (k) Olah, G. A.; Lapierre, J. C.; Carlson, C. G. *J. Org. Chem.* **1965**, *30*, 541−4. (l) Olah, G. A.; Lapierre, J. C. *J. Org. Chem.* **1966**, *31*, 1271−2. (m) Olah, G. A.; Lapierre, J. C.; McDonald, G. J. *J. Org. Chem.* **1966**, *31*, 1262−7. (n) Olah, G. A.; Lapierre, J. C.; Schreier, U. H. *J. Org. Chem.* **1966**, *31*, 1268−71. (o) Olah, G. A.; Olah, J. A. *J. Org. Chem.* **1967**, *32*, 1612−14.

(14) Wang, Z., Baddeley Isomerization. In *Comprehensive Organic Name Reactions and Reagents*; John Wiley & Sons, Inc.: New York, 2010.

(15) Olah, G. A. *Acc. Chem. Res.* **1971**, *4*, 240−8.

(16) (a) Kuck, D.; Matthias, C.; Barth, D.; Letzel, M. C. *Int. J. Mass Spectrom.* **2011**, *306*, 167−174. (b) Kolboe, S. *J. Phys. Chem. A* **2011**, *115*, 3106−3115. (c) Kolboe, S.; Svelle, S.; Arstad, B. *J. Phys. Chem. A* **2009**, *113*, 917−923. (d) Kolboe, S.; Svelle, S. *J. Phys. Chem. A* **2008**, *112*, 6399−6400. (e) Marcantoni, E.; Roselli, G.; Lucarelli, L.; Renzi, G.; Filippi, A.; Trionfetti, C.; Speranza, M. *J. Org. Chem.* **2005**, *70*, 4133−4141. (f) Lenoir, D. *Angew. Chem., Int. Ed.* **2003**, *42*, 854−857. (g) Filippi, A.; Roselli, G.; Renzi, G.; Grandinetti, F.; Speranza, M. *Chem.—Eur. J.* **2003**, *9*, 2072−2078. (h) Heidrich, D. *Angew. Chem., Int. Ed.* **2002**, *41*, 3208−3210. (i) Holman, R. W.; Eary, T.; Whittle, E.; Gross, M. L. *J. Chem. Soc., Perkin Trans. 2* **1998**, 2187−2194. (j) Berthomieu, D.; Audier, H.; Denhez, J. P.; Monteiro, C.; Mourgues, P. *Org. Mass Spectrom.* **1991**, *26*, 271−5.

(17) Kuck, D. *Int. J. Mass Spectrom.* **2002**, *213*, 101−144.

(18) (a) Myhre, P. C. *J. Am. Chem. Soc.* **1972**, *94*, 7921−3. (b) Hahn, R. C.; Strack, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 4335−7. (c) Gibbs, H. W.; Moodie, R. B.; Schofield, K. *J. Chem. Soc., Chem. Commun.* **1976**, 492−3. (d) Barnes, C. E.; Myhre, P. C. *J. Am. Chem. Soc.* **1978**, *100*, 973−5. (e) Barnes, C. E.; Myhre, P. C. *J. Am. Chem. Soc.* **1978**, *100*, 975−6. (f) Geppert, J. T.; Johnson, M. W.; Myhre, P. C.; Woods, S. P. *J. Am. Chem. Soc.* **1981**, *103*, 2057−62.

(19) (a) Al-Dosari, M. A. *Arabian J. Sci. Eng., Sect. A* **2010**, *35*, 7−17. (b) Al-Kinany, M. C.; Jibril, B. Y.; Al-Khowaiter, S. H.; Al-Dosari, M. A.; Al-Megren, H. A.; Al-Zahrani, S. M.; Al-Humaizi, K. I. *Chem. Eng. Process.* **2005**, *44*, 841−846. (c) Marques-Alvarez, H.; Silva, A. D.; Souza, P. H. G.; Constantino, A. M.; Hernandez-Valdes, R.; Aranda, D. A. G.; Antunes, O. A. C. *Catal. Commun.* **2004**, *5*, 221−224. (d) Takeuchi, G.; Shimoura, Y. *Catal. Surv. Jpn.* **1998**, *2*, 77−83. (e) Streitwieser, A., Jr.; Reif, L. *J. Am. Chem. Soc.* **1960**, *82*, 5003−5. (f) Streitwieser, A., Jr.; Downs, W. J. *J. Org. Chem.* **1962**, *27*, 625.

(20) (a) Cram, D. J. *J. Am. Chem. Soc.* **1949**, *71*, 3863−70. (b) Bachmann, W. E.; Ferguson, J. W. *J. Am. Chem. Soc.* **1934**, *56*, 2081−4.

(21) Allen, C. F. H.; Pingert, F. P. *J. Am. Chem. Soc.* **1942**, *64*, 1365−1371.

(22) Wynberg, H.; Wolf, A. P. *J. Am. Chem. Soc.* **1963**, *85*, 3308.

(23) Necula, A.; Racoveanu-Schiketanz, A.; Gheorghiu, M. D.; Scott, L. T. *J. Org. Chem.* **1995**, *60*, 3448−51.

(24) Sherman, S. C.; Iretskii, A. V.; White, M. G.; Gumienny, C.; Tolbert, L. M.; Schiraldi, D. A. *J. Org. Chem.* **2002**, *67*, 2034−2041.

(25) Racoveanu-Schiketanz, A.; Necula, A.; Gheorghiu, M. D.; Scott, L. T. *Tetrahedron Lett.* **1992**, *33*, 4119−22.

(26) Balaban, A. T.; Gheorghiu, M. D.; Schiketanz, A.; Necula, A. *J. Am. Chem. Soc.* **1989**, *111*, 734−5.

(27) (a) Balaban, A. T.; Farcasiu, D. *J. Am. Chem. Soc.* **1967**, *89*, 1958−60. (b) Balaban, A. T.; Farcasiu, D.; Koptyug, V. A.; Isaev, I. S.; Gorfinkel, M. I.; Rezvukhin, A. I. *Tetrahedron Lett.* **1968**, 4757−9. (c) Staab, H. A.; Haenel, M. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 548−9. (d) Staab, H. A.; Haenel, M. *Chem. Ber.* **1970**, *103*, 1095−100.

(28) (a) Dou, X.; Yang, X.; Bodwell, G. J.; Wagner, M.; Enkelmann, V.; Muellen, K. *Org. Lett.* **2007**, *9*, 2485−2488. (b) Ormsby, J. L.; Black, T. D.; Hilton, C. L.; Bharat; King, B. T. *Tetrahedron* **2008**, *64*, 11370−11378.

(29) Berthomieu, D.; Brenner, V.; Ohanessian, G.; Denhez, J. P.; Millie, P.; Audier, H. E. *J. Phys. Chem.* **1995**, *99*, 712−20.

(30) (a) Arstad, B.; Kolboe, S.; Swang, O. *J. Phys. Org. Chem.* **2004**, *17*, 1023−1032. (b) Arstad, B.; Kolboe, S.; Swang, O. *J. Phys. Org. Chem.* **2006**, *19*, 81−92.

(31) (a) Scholl, R.; Seer, C. *Ber. Dtsch. Chem. Ges. B* **1922**, *55B*, 109−17. (b) Scholl, R.; Seer, C. *Ber. Dtsch. Chem. Ges. B* **1922**, *55B*, 330−41. (c) Weitzenbock, R.; Seer, C. *Ber. Dtsch. Chem. Ges.* **1913**, *46*, 1994−2000. (d) Scholl, R.; Seer, C. *Justus Liebigs Ann. Chem.* **1913**, *394*, 111−77. (e) Scholl, R.; Seer, C. *Monatsh. Chem.* **1912**, *33*, 1−8. (f) Mullins, R. J.; Corbett, M. T. *Name React. Carbocyclic Ring Form.* **2010**, 409−422. (g) Scholl, R.; Seer, C.; Weitzenbock, R. *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 2202−9.

(32) Balaban, A. T.; Nenitzescu, C. D. Scholl and Related Reactions. In *Friedel−Crafts and Related Reactions. Vol. II. Alkylation and Related Reactions. Part 2*; Olah, G. A., Ed.; Interscience Publishers: New York, 1964; Vol. Chapter XXIII.

(33) (a) Jones, D. J.; Purushothaman, B.; Ji, S.; Holmes, A. B.; Wong, W. W. H. *Chem. Commun.* **2012**, *48*, 8066−8068. (b) Kivala, M.; Wu, D.; Feng, X.; Li, C.; Muellen, K. *Synth. Polym.* **2012**, *1*, 373−420. (c) Van Veller, B.; Schipper, D. J.; Swager, T. M. *J. Am. Chem. Soc.* **2012**, *134*, 7282−7285. (d) Mysliwiec, D.; Donnio, B.; Chmielewski, P. J.; Heinrich, B.; Stepien, M. *J. Am. Chem. Soc.* **2012**, *134*, 4822−4833. (e) Danz, M.; Tonner, R.; Hilt, G. *Chem. Commun. (Cambridge, U.K.)* **2012**, *48*, 377−379. (f) Cataldo, F.; Ursini, O.; Angelini, G.; Iglesias-Groth, S. *Fullerenes, Nanotubes, Carbon Nanostruct.* **2011**, *19*, 713−725. (g) Plunkett, K. N.; Godula, K.; Nuckolls, C.; Tremblay, N.; Whalley, A. C.; Xiao, S. *Org. Lett.* **2009**, *11*, 2225−2228. (h) Nagarajan, S.; Barthes, C.; Gourdon, A. *Tetrahedron* **2009**, *65*, 3767−3772.

(34) (a) Zhai, L.; Shukla, R.; Rathore, R. *Org. Lett.* **2009**, *11*, 3474−3477. (b) King, B. T.; Kroulik, J.; Robertson, C. R.; Rempala, P.; Hilton, C. L.; Korinek, J. D.; Gortari, L. M. *J. Org. Chem.* **2007**, *72*, 2279−2288. (c) Rempala, P.; Kroulik, J.; King, B. T. *J. Org. Chem.* **2006**, *71*, 5067−5081. (d) Rempala, P.; Kroulik, J.; King, B. T. *J. Am. Chem. Soc.* **2004**, *126*, 15002−15003. (e) Tanaka, M.; Nakashima, H.; Fujiwara, M.; Ando, H.; Souma, Y. *J. Org. Chem.* **1996**, *61*, 788−92.

(35) Cho, H. Y.; Ajaz, A.; Himali, D.; Waske, P. A.; Johnson, R. P. *J. Org. Chem.* **2009**, *74*, 4137−4142.

(36) (a) Bakoss, H. J.; Roberts, R. M. G.; Sadri, A. R. *J. Org. Chem.* **1982**, *47*, 4053−5. (b) Roberts, R. M. G. *J. Org. Chem.* **1982**, *47*, 4050−3.

(37) Olah, G. A., Surya Prakash, G. K., Molnar, A., Sommer, J., Eds. *Superacid Chemistry*, 2nd ed.; Wiley-Interscience: New York, 2009; 850 pp.

(38) Kutt, A.; Rodima, T.; Saame, J.; Raamat, E.; Maemets, V.; Kaljurand, I.; Koppel, I. A.; Garlyauskayte, R. Y.; Yagupolskii, Y. L.; Yagupolskii, L. M.; Bernhardt, E.; Willner, H.; Leito, I. *J. Org. Chem.* **2011**, *76*, 391−395.

(39) Bos, M.; Dahmen, E. A. M. F. *Anal. Chim. Acta* **1973**, *63*, 185−96.

(40) (a) Reid, C. *J. Am. Chem. Soc.* **1954**, *76*, 3264−8. (b) Dallinga, G.; Mackor, E. L.; Verrijn Stuart, A. A. *Mol. Phys.* **1958**, *1*, 123−40. (c) Hammonds, M.; Pathak, A.; Sarre, P. J. *Phys. Chem. Chem. Phys.* **2009**, *11*, 4458−4464. (d) Alata, I.; Omidyan, R.; Broquier, M.; Dedonder, C.; Dopfer, O.; Jouvet, C. *Phys. Chem. Chem. Phys.* **2010**, *12*, 14456−14458. (e) Garkusha, I.; Fulara, J.; Nagy, A.; Maier, J. P. *Astrophys. J.* **2011**, *728*, 131/1−131/7.

(41) Spartan 06 and Spartan 08; Wavefunction Inc., Irvine, CA.

(42) (a) Frisch, M. J.; et al. Gaussian 03, Revision E.01; Gaussian Inc., Wallingford, CT, 2004. (b) Frisch, M. J.; et al. Gaussian 09, Revision B.01; Gaussian Inc., Wallingford, CT, 2010.

(43) (a) Aue, D. H. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2011**, *1*, 487−508. (b) Lodewyk, M. W.; Gutta, P.; Tantillo, D. J. *J. Org. Chem.* **2008**, *73*, 6570−6579.

(44) Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999−3094.

(45) Olah, G. A.; Schlosberg, R. H.; Porter, R. D.; Mo, Y. K.; Kelly, D. P.; Mateescu, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 2034−43.

(46) Glukhovtsev, M. N.; Pross, A.; Nicolaides, A.; Radom, L. *J. Chem. Soc., Chem. Commun.* **1995**, 2347−8.
(47) (a) Lima, C. F. R. A. C.; Rocha, M. A. A.; Melo, A.; Gomes, L. R.; Low, J. N.; Santos, L. M. N. B. F. *J. Phys. Chem. A* **2011**, *115*, 11876−11888. (b) Padwa, A.; Brodsky, L.; Clough, S. *J. Am. Chem. Soc.* **1972**, *94*, 6767−75.
(48) (a) Zhang, S.-L.; Xue, Z.-F.; Gao, Y.-R.; Mao, S.; Wang, Y.-Q. *Tetrahedron Lett.* **2012**, *53*, 2436−2439. (b) Ghanbaripour, R.; Mohammadpoor-Baltork, I.; Moghadam, M.; Khosropour, A. R.; Tangestaninejad, S.; Mirkhani, V. *Polyhedron* **2012**, *31*, 721−728. (c) Ono, F.; Ishikura, Y.; Tada, Y.; Endo, M.; Sato, T. *Synlett* **2008**, 2365−2367. (d) Clapp, D. B.; Morton, A. A. *J. Am. Chem. Soc.* **1936**, *58*, 2172. (e) Bernhauer, K.; Muller, P.; Neiser, F. *J. Prakt. Chem. (Leipzig)* **1936**, *145*, 301−8.