sionally determined by HPLC after addition of an appropriate amount of a 1,2-dichloroethane stock solution of *erythro*-1,2-dibromo-1-phenylpropane, obtained by bromination of *trans*-1-phenylpropene with tetrabutylammonium tribromide in 1,2-dichloroethane and crystallized from chloroform, mp 63–65 °C. In complete reactions the dibromide yields amounted to 95–100%.

Several runs (3, 4, 7, and 13 of Table I) were monitored at different times during the course of the reactions by sample withdrawal and HPLC analysis.

The bromination of *trans*- and *cis*-stilbene in nitromethane was carried using a procedure identical with that described above for bromination in 1,2-dichloroethane.

The stability of dibromides **3** and **4** in the presence of Br_2 was checked by exposing both dibromides (10^{-2} to 10^{-4} M) to a 10- to 50-fold excess of Br_2 in 1,2-dichloroethane at 25 °C for 3 h, followed by HPLC analysis.

Product Analysis. The product distributions were determined by HPLC using a 25-cm Hypersil 10 C18 column (HPLC technology) and UV detector (λ 240 nm), with methanol–water (70:30 v/v) as the eluant at a flow rate of 1.5 mL/min. The reaction mixtures were directly injected after appropriate dilution. The product ratios and the yields were respectively determined by using calibration curves obtained with the pure dibromides and olefins, and the standard. The dibromides distributions reported in Table I are the averages of triplicate runs and were reproducible to ±1%.

Kinetic Measurements. Bromine solutions in 1,2-dichloroethane were prepared shortly before use and stored in the dark for no longer than 3–4 h. Their concentrations were determined from the Br_2 absorption (ϵ_{max} 211 M^{-1} cm^{-1} at λ_{max} 409 nm) and adjusted to twice the desired initial concentrations in the kinetic runs. Aliquots of these solutions were prethermostated at 25 °C (±0.05 °C) and mixed with an equal volume of prethermostated solutions of *cis*-stilbene of suitable concentration, prepared by weighing. The fastest reaction (run 1 of Table II) was carried out with a stopped-flow instrument equipped with a 2-cm observation cell, monitoring the disappearance of Br_2 at 530 nm (ϵ 34 M^{-1} cm^{-1}). Runs 2 and 3 of Table I were carried out in 4-cm cells using a conventional UV–vis spectrophotometer and monitoring the disappearance of Br_2 at 409 nm. Run 4 of Table II was followed by withdrawing from the reaction mixture samples of exactly known volume, which were treated with a saturated solution of Na_2SO_3 to reduce the excess Br_2. An appropriate amount of a 1,2-dichloroethane solution of *erythro*-1,2-dibromo-1-phenylpropane was added to each sample, and the amounts of unreacted olefins and formed dibromides were determined by HPLC under the above reported conditions. The data in runs 1 and 2, in run 3, and in run 4 of Table II were respectively fitted to the third-order, pseudo-second-order, and pseudo-first-order rate equation. In the last two cases third-order rate constants were calculated from the pseudo-second- and pseudo-first-order constants assuming an overall third-order dependence of the rate. The k_3 values are reported in Table II.

Acknowledgment. This work was supported by a grant from the Consiglio Nazionale delle Ricerche and from the Ministero della Pubblica Istruzione. We thank Dr. Roberto Ambrosetti (Istituto di Chimica Quantistica ed Energetica Molecolare del CNR, Pisa) for helpful discussion.

Registry No. 1, 645-49-8; 2, 103-30-0; 3, 13440-24-9; (±)-4, 13027-48-0; *erythro*-$Ph(CH(Br))_2CH_3$, 127154-65-8; *trans*-$PhCH{=}CHCH_3$, 873-66-5; tetrabutylammonium tribromide, 38932-80-8.

Interplay between Conjugative and Steric Effects in Cyclopropylarenes

R. E. Drumright, R. H. Mas, J. S. Merola,* and J. M. Tanko*

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061-0212

Received December 20, 1989

The X-ray crystal structures of three cyclopropylarenes are reported. The data suggest that, for the series phenyl → α-naphthyl → 9-anthryl, increasing steric interactions force a distortion from the normally preferred bisected conformation to the perpendicular conformation. In the bisected conformation, orbital alignment between the aromatic π-system and the cyclopropyl HOMO is maximal and electron donation from the cyclopropyl to the arene can be detected by an asymmetry in the lengths of the vicinal and distal C–C bonds of the cyclopropane ring. In the perpendicular conformation, the π-system of the arene is orthogonal to the HOMO, but aligned with the LUMO of the cyclopropyl group. Consequently, the cyclopropyl group can only act as an electron acceptor. Within experimental error, there was no apparent asymmetry in the lengths of the vicinal and distal C–C bonds, suggesting no significant electronic interaction between the arene and the cyclopropyl group in the perpendicular conformation.

Introduction

The structure and chemistry of cyclopropane derivatives have intrigued chemists for decades. Possessing both alkanic and alkenic properties, the cyclopropyl group has found a unique niche in functional group chemistry.[1] The Walsh (Sugden) model[2] envisages that cyclopropane is "built" from three sp^2-hybridized CH_2's, with the sp^2 hybrids oriented radially toward the center of the three-membered ring and the three p orbitals coplanar (Figure 1).

When attached to a π-system, the cyclopropyl substituent is a good π-electron donor. It is well-founded, in both theory and experiment, that these π-donor properties of the cyclopropyl group are conformation-dependent. Because of the π-symmetry associated with the highest occupied molecular orbital (3e′) of the cyclopropyl group, interaction with an adjacent π-system is maximal when the orbitals are coplanar (i.e., "bisected" conformation **1**). In the alternative "perpendicular" conformation **2**, the HOMO of the cyclopropyl group is orthogonal to the π-system and the interaction is minimal.[3,4]

(1) Rappoport, Z., Ed. *The Chemistry of the Cyclopropyl Group, Parts 1 and 2*; Wiley: New York, 1987. Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978.

(2) Walsh, A. D. *Nature (London)* **1947**, *159*, 167, 712. Walsh, A. D. *Trans. Faraday Soc.* **1949**, *45*, 179. Sugden, T. M. *Nature (London)* **1947**, *160*, 367.

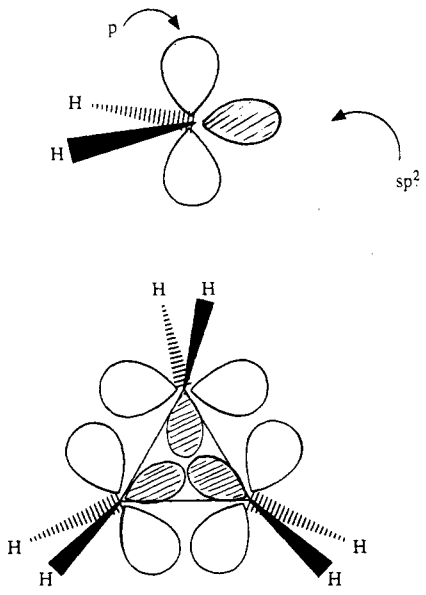


Figure 1. Walsh (Sugden) model for cyclopropane.

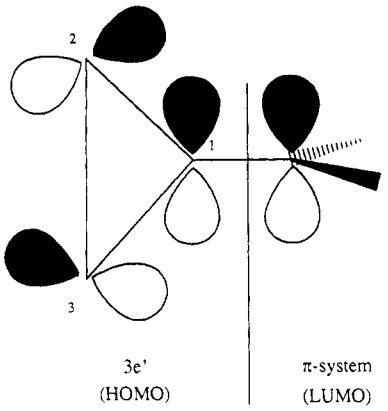


Figure 2. Donor-acceptor interaction between a cyclopropyl group and a π-system (bisected conformation).

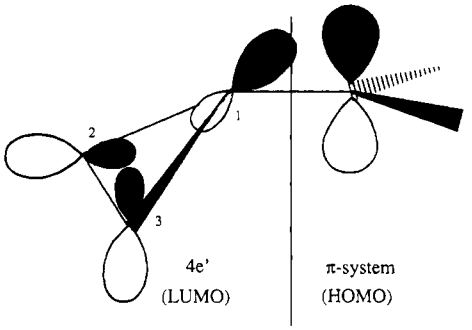
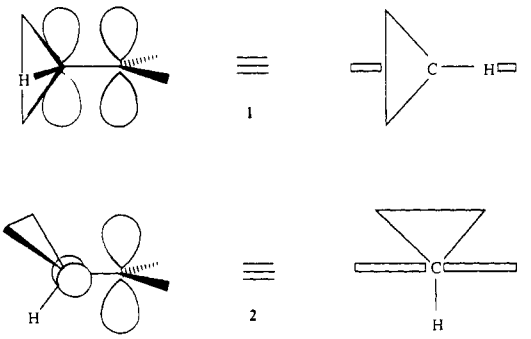


Figure 3. Donor-acceptor interactions between a cyclopropyl group and a π-system (perpendicular conformation).

Table I. Conformational Equilibria in Cyclopropylarenes

system	conformational equilibrium[a]	ΔE,[b] kcal/mol	$\Delta E^{\ddagger}$,[b] kcal/mol
phenyl	bisected → perpendicular	1.1	1.2
α-naphthyl	perpendicular[c] → BI-ANTI	1.2	1.4
	perpendicular[c] → BI-SYN	5.2	8–9
9-anthryl	perpendicular → bisected	9.7	12

[a] Lowest energy conformation appears on the left side of equation. [b] Calculated MMX; see ref 8. [c] For the "perpendicular" conformation of α-cyclopropylnaphthalene, the angle between the cyclopropylmethine C-H bond and the aromatic plane was 67.5°, 22.5° displaced from the true perpendicular (see Figure 4).



For the bisected conformation, the degree of interaction between the cyclopropyl group and the π-system is revealed by the lengths of the vicinal (C_1–C_2, C_1–C_3) and distal (C_2–C_3) bonds of the cyclopropyl ring. Transfer of electron density from the 3e′ orbital decreases both the bonding character between C_1–C_2 and C_1–C_3 and the antibonding character between C_2–C_3, resulting in a net lengthening of the vicinal bonds and shortening of the distal bond (Figure 2).[5]

In the perpendicular conformation, the cyclopropyl group can function as a weak π-acceptor. Donation of electron density to the 4e′ LUMO is predicted to result in the lengthening and shortening of the vicinal and distal bonds, respectively (Figure 3). Stabilization of cyclopropane by π-donors is expected to be important only for potent π-donors.[5]

The nature and degree of interaction between the aryl and cyclopropyl groups of a cyclopropylarene are not straightforward. In a survey of 146 X-ray crystal structures of a variety of substituted cyclopropanes, Allen suggests that a phenyl group acts as an electron acceptor in the bisected conformation but may be a π-donor in the perpendicular conformation in cyclopropylarenes. However, this database did not include any simple aryl-substituted cyclopropanes (e.g., Ar-c-C_3H_5).[6]

In 1987, the X-ray crystal structure of phenylcyclopropane was reported.[7] This molecule was found to adopt the bisected conformation. The vicinal bonds were longer than the distal (1.520 vs 1.502 Å), further augmenting the argument that the cyclopropyl was serving as a π-donor to the aromatic.

Using X-ray crystallography and molecular mechanics calculations, we have explored the interplay between steric and conjugative effects for the unsubstituted cyclopropyl group (c-C_3H_5) attached to three aromatic moieties: phenyl, α-naphthyl, and 9-anthryl.

Results

Molecular Mechanics Calculations. In order to assess the role of steric effects in the cyclopropylarenes, molecular mechanics calculations[8] were performed on phenylcyclopropane, α-cyclopropylnaphthalene, and 9-cyclopropylanthracene, the results of which are summarized in Table I. For each of the conformational equilibria depicted, ΔE refers to the energy difference between the

(3) Jorgensen, W. C.; Salem, L. *The Organic Chemist's Book of Orbitals*; Academic Press: New York, 1973.
(4) Hoffman, R. *Tetrahedron Lett.* **1970**, 2907. Hoffman, R.; Davidson, R. B. *J. Am. Chem. Soc.* **1971**, *93*, 5699.
(5) Clark, T.; Spitznagel, G. W.; Klose, R.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1984**, *106*, 4412.
(6) Allen, F. H. *Acta Crystallogr.* **1980**, *B36*, 81. See also: Allen, F. H., Kennard, O.; Taylor, R. *Acc. Chem. Res.* **1983**, *16*, 146.
(7) de Boer, J. S. A. M.; Loopstra, B. O.; Stam, C. H. *Recl. Trav. Chim. Pays-Bas* **1987**, *106*, 537.
(8) MMX, Serena Software, Bloomington, IN 47402-3076. This program is derived from MM2 (QCPE 395) with MMP1 π-subroutines included and is run on either an IBM PS/2 Model 50 or VAX 8800.

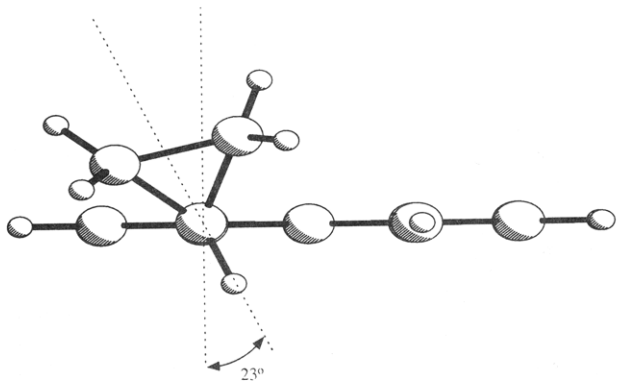
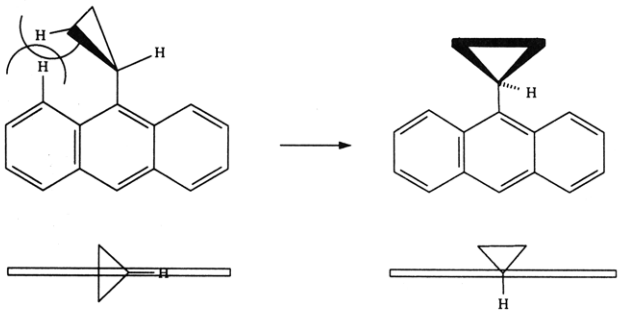


Figure 4. Lowest energy conformation of α-cyclopropylnaphthalene (MM2).

two conformations. The barrier to interconversion, $\Delta E^{\ddagger}$ was calculated employing the dihedral angle driver facility and rotating through the dihedral in 10° increments.

For phenylcyclopropane, the cyclopropyl group is essentially freely rotating with a slight (1.1 kcal/mol) preference for the bisected conformation. This result is in reasonable accord with the experimental value of 1.4 kcal/mol, obtained from ^{1}H NMR spectroscopy.[9]

For the 9-anthryl derivative, unfavorable peri interactions with the *cis*-hydrogens of the cyclopropyl destabilize the bisected conformation (relative to the perpendicular) by 9.7 kcal/mol. Because of this large energy difference and the correspondingly large barrier to rotation (12 kcal/mol), 9-cyclopropylanthracene appears to be effectively "locked" in the perpendicular conformation.



For the α-naphthyl derivative, two nondegenerate bisected conformations are found, BI-SYN and BI-ANTI. Because of peri interactions analogous to those present in the 9-anthryl system, BI-SYN is strongly disfavored. In addition, these peri interactions also prevent the molecule from achieving a truly perpendicular conformation. In the lowest energy conformation, the cyclopropyl group is predicted to be twisted ca. 23° from the true perpendicular (Figure 4).

BI-SYN BI-ANTI

X-ray crystal structures were determined for three arylcyclopropanes: the (2,4-dinitrophenyl)hydrazine derivative of *p*-cyclopropylacetophenone, 4-cyclopropyl-1-naphthalenecarboxylic acid, and 9-chloro-10-cyclopropylanthracene. The conformations of the molecules observed in the solid state parallel the molecular mechanics assessments, and their ORTEP plots are presented in Figure 5. The angle θ is defined by the midpoint of the distal C–C bond and the plane of the aromatic ring (i.e., θ = 0° for the bisected conformation and 90° for the perpendicular). Table II summarizes the relevant bond lengths determined for each system.

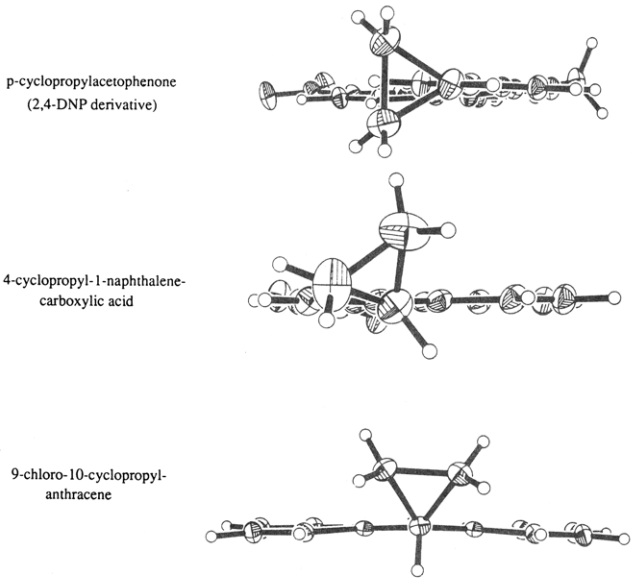


Figure 5. ORTEP plots of various cyclopropylarenes.

Table II. Summary of Important Bond Lengths (Å)

compound	vicinal C–C	distal C–C	arene–Cp
p-cyclopropylacetophenone (2,4-DNP deriv)	1.492 (4), 1.481 (5)	1.457 (5)	1.471 (4)
4-cyclopropyl-1-naphthalene-carboxylic acid	1.455 (7), 1.463 (7)	1.445 (7)	1.498 (5)
9-chloro-10-cyclopropylanthracene	1.498 (5), 1.500 (4)	1.491 (5)	1.503 (4)

The phenyl derivative adopts the bisected conformation (θ = 0.6°). This conformational preference for phenylcyclopropane has also been previously demonstrated experimentally by X-ray crystallography[7] as well as by a variety of other techniques.[9–11]

For the 9-anthryl derivative, the perpendicular conformation (θ = 88°) is observed in the solid state. This result is also in accord with the molecular mechanics predictions.

For the α-naphthyl system, molecular mechanics calculations predict (within a 180° arc) a freely rotating cyclopropyl with a slight preference for an intermediate conformation (θ = 67°). The X-ray structure confirms this prediction, indicating the preferred conformation to be midway between the perpendicular and bisected conformations (θ = 54°). We suggest for this system that this conformation lies at a potential energy minimum, minimizing unfavorable steric effects while maintaining some degree of overlap between the cyclopropyl and aromatic rings. (Note: The molecular mechanics calculations do not account for any type of conjugative interaction between the two ring systems). Consequently, it may be reasonable to suppose that this conformation, which represents a

(9) Closs, G. L.; Klinger, H. B. *J. Am. Chem. Soc.* **1966**, *87*, 3265.

(10) Hahn, R. C.; Howard, P. H.; Kong, S.-M.; Lorenzo, G. A.; Miller, N. L. *J. Am. Chem. Soc.* **1969**, *91*, 3558 and references therein.

(11) Jason, M. E.; Kurzweil, P. R.; Leonard, K. E. *J. Org. Chem.* **1986**, *51*, 2551 and references therein.

Table III. Bond Length Distortions in Cyclopropylarenes as a Function of Conformation

aryl gp	θ,[a] deg	r_{C-C}(vic, av) − r_{C-C}(dist), Å	ref
phenyl	0	0.018	7
	0.6	0.030	this work
α-naphthyl	54	0.014	this work
9-anthryl	88	0.008	this work

[a] See text for explanation.

compromise between steric and electronic effects, would be the lowest energy conformer in this system.

Discussion

The relative π-acceptor properties of the various arenes, and the possible perturbation of these properties by substituents, were assessed by examining the calculated atomic charge at the CH_2 group of the corresponding arylmethyl anions ($ArCH_2^-$). These formal charges were obtained from semiempirical molecular orbital calculations, using the AM1 approximation.[12] For the series phenyl → α-naphthyl → 9-anthryl, the charge at the CH_2 of $ArCH_2^-$ decreases from −0.525 → −0.445 → −0.376, suggesting a π-acceptor order: 9- anthryl > α-naphthyl > phenyl. Further, the introduction of substituents analogous to those present in the compound utilized in this study does not alter this relative order.

For the three cyclopropylarenes examined, the vicinal C–C bonds were found to be longer than the distal (Table III). However, the differences in these bond lengths decreased in the series phenyl (θ = 0°) → α-naphthyl (θ = 54°) → 9-anthryl (θ = 88°). This trend supports the notion that the cyclopropyl's π-donor properties become attenuated as it is rotated from the bisected to perpendicular conformations.

For the anthryl derivative, the two vicinal and distal bond lengths (Å) are 1.500 (±0.004), 1.498 (±0.005), and 1.491 (±0.005), respectively, possibly suggesting some nominal electronic interaction between the anthryl and cyclopropyl rings, presumably with the cyclopropyl serving as a π-acceptor. However, within experimental error, these bond lengths are equivalent.

We therefore conclude that, for cyclopropylarenes in the perpendicular conformation, the π-donor properties of cyclopropane have been effectively "switched off". Any π-acceptor properties of the cyclopropyl in this conformation are nominal, resulting in bond length distortions below our limit of detection.

Experimental Section

General Procedures. Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected. Nuclear magnetic resonance spectra were recorded on a 270-MHz Bruker FT NMR spectrometer. All chemical shifts are reported in δ units, relative to $(CH_3)_4Si$ (δ 0.00). Infrared spectra were recorded on a Perkin-Elmer Model 710B spectrometer. Mass spectral data were obtained from a Varian MAT 112 instrument. Semiempirical calculations on the arylmethyl anions were performed with the AM1 approximation developed by Dewar et al.[12] and implemented through MOPAC, Version 5.0 (QCPE 455), with full geometry optimization.

X-ray Crystal Structure Determinations. For all three structures reported in this paper, the single-crystal X-ray diffraction studies were carried out on a Nicolet R3/mV four-circle diffractometer employing graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). All determinations were performed at room temperature, and all calculations were done with use of the Shelxtl Plus package of programs as supplied by Nicolet Corp.

(2,4-Dinitrophenyl)hydrazone of *p*-Cyclopropylacetophenone. To 1.0 g (5.1 mmol) of (2,4-dinitrophenyl)hydrazine in a 50-mL flask was added 5 mL of concentrated sulfuric acid. Water (7.5 mL) was added dropwise with stirring. Stirring was continued until solution was complete, and then 25 mL of 95% ethanol was added. In a second flask, 1.0 g (6.3 mmol) of *p*-cyclopropylacetophenone, prepared by the acylation of phenylcyclopropane according to the published procedures of Hart and Levitt,[13] was dissolved in 25 mL of 95% ethanol. The freshly prepared (2,4-dinitrophenyl)hydrazine solution was then poured into the flask containing the ketone, and the resulting mixture was allowed to stand at room temperature for 30 min. The red/orange solid was collected and dried (mp 223–224 °C). Crystals suitable for X-ray diffraction were obtained by slow evaporation of a stoppered solution of the hydrazone in chloroform. A single crystal of approximate dimensions 0.4 × 0.6 × 0.8 mm was chosen for this study. Crystal data for $C_{17}H_{16}N_4O_4$: monoclinic, space group $P2_1/n$ with a = 6.969 (5) Å, b = 15.603 (9) Å, c = 14.597 (5) Å, β = 98.75 (5)°, V = 1569 (2) Å^3, Z = 4, d_{calcd} = 1.44 g cm^{-3}, and fw = 340.3. A total of 3149 reflections were collected by the $\theta/2\theta$ scan method employing a 1.2° scan range (ω) and scan speeds varying from 3 to 15° min^{-1} in the 2θ range 3.5–50°. Of these, 2778 were unique with 2421 ($F > 3.0\sigma(F)$) observed reflections employed in the refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods. All non-hydrogen atoms were refined anisotropically while hydrogen atoms were placed at calculated positions and treated with a riding model with fixed isotropic U. A unit weighting scheme was employed in the refinement, yielding final R = 5.11% and R_w = 4.82%. The data to parameter ratio was 10.7:1.

4-Cyclopropyl-1-naphthalenecarboxylic Acid. A 25-mL flask fitted with condenser, addition funnel, and magnetic stirrer was charged with magnesium (40 mg, 1.7 mmol). The system was flame-dried while a fast current of nitrogen passed through the apparatus. After cooling, one very small crystal of iodine was added and the system was heated with a flame until purple vapors were visible. After cooling, 2 mL of a solution of 1-bromo-4-cyclopropylnaphthalene (296 mg, 1.2 mmol), prepared by treatment of α-cyclopropylnaphthalene with Br_2/Fe, in 10 mL of dry ether was added in one portion to the flask. After initiation of the reaction, the remainder of the aryl bromide solution was added dropwise. The reaction mixture was refluxed for 30 min and then allowed to cool to room temperature. Several small pieces of dry ice were then added. After the mixture was warmed to room temperature, 5 mL of 15% HCl was added slowly. The layers were separated, and the organic layer was treated with 5 mL of 50% sodium hydroxide solution. The aqueous layer was separated and acidified with concentrated hydrochloric acid, and a white precipitate formed. Filtration and drying yielded 210 mg (82%) of 4-cyclopropyl-1-naphthoic acid: mp 169–170 °C; ^{1}H NMR ($CDCl_3$) δ 0.9 (m, 2 H), 1.2 (m, 2 H), 2.4 (m, 1 H), 7.3 (d 1 H), 7.7 (m, 2 H), 8.4 (d, 1 H), 8.6 (dd, 1 H), 9.2 (dd, 1 H). Crystals suitable for X-ray diffraction were obtained by slow evaporation of a stoppered solution of the acid in chloroform. A single crystal of approximate dimensions 0.4 × 0.6 × 0.2 mm was chosen for this study. Crystal data for $C_{14}H_{12}O_2$: monoclinic, space group $C2/c$ with a = 18.063 (7) Å, b = 7.612 (3) Å, c = 16.931 (7) Å, β = 111.66 (3)°, V = 2163.7 (15) Å^3, Z = 8, d_{calcd} = 1.303 g cm^{-3}, and fw = 212.2. A total of 1607 reflections were collected by the $\theta/2\theta$ scan method employing a 1.2° scan range (ω) and scan speeds varying from 3 to 15° min^{-1} in the 2θ range 3.5–50°. Of these, 1419 were unique with 1221 ($F > 3.0\sigma(F)$) observed reflections employed in the refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods. All non-hydrogen atoms were refined anisotropically while hydrogen atoms were placed at calculated positions and treated with a riding model with fixed isotropic U. A unit weighting scheme was employed in the refinement, yielding final R = 5.99% and R_w =

(12) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(13) Hart, H.; Levitt, G. *J. Org. Chem.* **1959**, *24*, 1261.

4.96%. The data to parameter ratio was 8.4:1.

9-Chloro-10-cyclopropylanthracene. Chlorine (1.55 mmol) was condensed into a 30-mL pressure tube containing 9-cyclopropylanthracene[14] (0.34 g, 1.6 mmol), anhydrous K_2CO_3 (0.22 g, 1.6 mmol), and 5 mL of carbon tetrachloride. The pressure tube was wrapped with aluminum foil and placed in a water bath maintained at 15 °C. After 1 h, the reaction mixture was filtered and the resulting filtrate concentrated on a rotary evaporator. The residue was purified by column chromatography (neutral alumina, 97:3 hexane-CH_2Cl_2). Recrystallization from ethanol afforded 0.25 g (65%) of the desired product, mp 117-118 °C; ^{1}H NMR ($CDCl_3$) δ 0.79 (m, 2 H, *cis*-cyclopropylmethylene H), 1.47 (m, 2 H, *trans*-cyclopropylmethylene H), 2.47 (m, 1 H, cyclopropylmethine), 7.51-7.61 (m, 4 H, 2-, 3-, 6-, and 7-H of anthryl), 8.69 (m, 2 H, 1- and 8-H of anthryl), 8.78 (m, 2 H, 4- and 5-H of anthryl); ^{13}C NMR ($CDCl_3$) δ 9.64 and 10.67 (cyclopropyl C), 121.78, 125.22, 126.29, 128.25, 128.65, 132.25 and 134.56 (anthryl C); MS (EI, 70 eV) *m/e* (relative intensity) 254 (14, M + 2), 252 (40, M^+), 217 (100), 215 (55), 202 (68), 108 (13), 101 (12), 95 (11). Anal. Calcd for $C_{13}H_{13}Cl$: C, 80.79; H, 5.15; Cl, 14.06. Found: C, 80.40; H, 5.19; Cl, 14.15. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a stoppered solution of the anthracene in acetonitrile. A single crystal of approximate dimensions 0.3 × 0.4 × 0.4 mm was chosen for this study. Crystal data for $C_{17}H_{13}Cl$: orthorhombic, space group $P2_12_12_1$ with a = 4.890 (2) Å, b = 14.698 (6) Å, c = 17.097 (7) Å, V = 1228.9 (9) Å^3, Z = 4, d_{calcd} = 1.366 g cm^{-3}, and fw = 252.7. A total of 1691 reflections were collected by the $\theta/2\theta$ scan method employing a 1.2° scan range (ω) and scan speeds varying from 3 to 15° min^{-1} in the 2θ range 3.5-45°. Of these, 1636 were unique with 1272 ($F > 3.0\sigma(F)$) observed reflections employed in the refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods. All non-hydrogen atoms were refined anisotropically while hydrogen atoms were placed at calculated positions and treated with a riding model with fixed isotropic U. A weighting scheme with ($w^{-1} = \sigma^2(F) + 0.0002F^2$) was employed in the refinement, and the data were corrected for extinction, yielding final R = 4.31% and R_W = 4.34%. The data to parameter ratio was 7.8:1.

(14) Bauld, N. L.; McDermed, J. D.; Hudson, C. E.; Rim, Y. S.; Zoeller, J., Jr.; Gordon, R. D.; Hyde, J. J. *J. Am. Chem. Soc.* **1969**, *91*, 6666.

Acknowledgment. We gratefully acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Jeffress Trust Fund, and the Department of Chemistry at Virginia Tech for financial support.

Supplementary Material Available: Labeled ORTEP plots, experimental details of the X-ray diffraction experiments, tables of final atomic positional parameters, atomic thermal parameters, and bond distances and angles from the X-ray structural determinations of the (2,4-dinitrophenyl)hydrazone of *p*-cyclopropylacetophenone, 4-cyclopropyl-1-naphthalenecarboxylic acid, and 9-chloro-10-cyclopropylanthracene (27 pages). Ordering information is given on any current masthead page.

The Use of Bis(4-chlorophenyl) Selenide/Lewis Acid Catalysts in the Electrophilic Chlorination of Toluene

John C. Graham,* Chung-Hwa Feng,[1] Margarita Orticochea,[2] and Gulam Ahmed[3]

Coatings Research Institute, Eastern Michigan University, Ypsilanti, Michigan 48197

Received December 5, 1989

The electrophilic chlorination of toluene has been studied using bis(4-chlorophenyl) selenide/Lewis acids as catalysts. These catalysts generate ortho/para ratios which are considerably lower than those obtained using Lewis acids as catalysts with the ortho/para ratio decreasing as the reaction temperature increases in the range of -30 to 70 °C. The enhanced para selectivity observed using these catalysts has been ascribed to the intermediacy of a bis(4-chlorophenyl)selenium dichloride/Lewis acid complex which functions as a sterically hindered source of chlorine. Proton NMR studies in acetone-d_6 support the existance of bis(4-chlorophenyl)selenium dichloride/Lewis acid complexes which lose chlorine directly from the selenium atom. The loss of para selectivity as the reaction temperature decreases has been ascribed to an increase in the conversion of bis(4-chlorophenyl) selenide to bis(4-chlorophenyl)(4-methylphenyl)selenonium chloride, which does not function as a catalyst in this reaction. Although triarylselenonium chlorides are known to reductively eliminate to produce aryl chlorides, our studies have shown that only where the Lewis acid is aluminum(III) chloride does this occur. Subsequently, with the exception of aluminum(III) chloride, reductive elimination of bis(4-chlorophenyl)(4-methylphenyl)-selenonium chloride is not responsible for the high para selectivity observed under our conditions.

Introduction

The electrophilic chlorination of aromatic compounds such as toluene historically has involved the use of Lewis acid catalysts such as aluminum(III) chloride, iron(III) chloride, or antimony(V) chloride. These catalysts, in the case of toluene, generate a statistical mixture of *o*-chlorotoluene and *p*-chlorotoluene as well as minor amounts of *m*-chlorotoluene and polychlorotoluenes. In actual practice, the reaction appears to be quite complex with the product distribution varying widely depending on the reaction media, temperature, and nature of the chlorinating agent.[1-22] For example, Stock and Himoe[5]

(1) Feng, C. H. M.S. Thesis, Eastern Michigan University, August 1988.
(2) Orticochea, M. M.S. Thesis, Eastern Michigan University, April 1989.
(3) Ahmed, G. M.S. Thesis, Eastern Michigan University, December 1988.

(4) Olah, G. *Friedel Crafts Chemistry*; J. Wiley & Sons: New York, 1973; p 509.
(5) Stock, L. M.; Himoe, A. *J. Am. Chem. Soc.* **1961**, *83*, 4605.
(6) Hugust, X. P.; Ylla-Catala, A. *Afinidad* **1964**, *20* (229), 15; *Chem. Abstr.* **1964**, *60*, 15700d:
(7) Stock, L. M.; Himoe, A. *Tetrahedron Lett.* **1960**, *13*, 9.
(8) De La Mare, P. D. B.; Robertson, P. W. *J. Chem. Soc.* **1943**, 279.
(9) Robertson, P. W. *J. Chem. Soc.* **1954**, 1267.
(10) Keefer, R. M.; Andrews, L. J. *J. Am. Chem. Soc.* **1957**, *79*, 4348.
(11) Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* **1960**, *82*, 5823.