Some Generalizations Concerning the Reactivity of Aryl Positions Adjacent to Fused Strained Rings

Sir:

A variety of qualitative and some quantitative observations relate to the relative reactivities of aryl positions adjacent to fused strained rings in an area of chemistry that dates back to the Mills–Nixon effect.[1] To this chemistry we contribute the kinetic data summarized in Table I. Procedures for the base-catalyzed protodetritiations are detailed in our recent papers. In the older lithium cyclohexylamide (LiCHA) runs the base concentration was used to calculate a second-order rate constant which was compared to that for benzene in deriving a relative rate. In the recent runs the kinetic mixture contained at least two components so that relative rates are derived directly, without reference to the catalyst concentration. The protodetritiations in trifluoroacetic acid were derived from the work of Eaborn, *et al.*[2] From these kinetic results, combined with other observations, a consistent pattern emerges which we propose to generalize and interpret.

Table I. Protodetritiation Kinetics

Hydrocarbon	Reagent[a]	Temp, °C	10^5k, sec^{-1}	k_T/k_{PhT}
Biphenylene-1-*t* Toluene-*α*-*t*	LiCHA	50.0	19 ± 1 3.8 ± 0.2	490 (100)[b]
Biphenylene-2-*t*	0.061 *M* LiCHA	49.9	0.26 ± 0.03	~7.7
Biphenylene-2-*t* *p*-Xylene-*α*-*t*	LiCHA	50.0	0.200 ± 0.008 1.01 ± 0.03	6.2 (31)[b,c]
Benzo[*b*]biphenylene-5-*t*	0.060 *M* LiCHA	49.9	~55[d]	~1600
Benzo[*b*]biphenylene-5-*t*	0.060 *M* LiCHA	49.9	72.6 ± 1.0	2130
Triptycene-1-*t* Benzene-*t*	CsCHA	25.0	12.8 ± 0.4 0.619 ± 0.010	20.7
Triptycene-1-*t* Benzene-*t*	CsCHA	25.0	7.21 ± 0.22 0.349 ± 0.018	20.8
Triptycene-2-*t* Benzene-*t*	CsCHA	25.0	2.17 ± 0.005 0.783 ± 0.043	2.77
Triptycene-1-*t*	CF_3COOH[e]	70.0	0.0448 ± 0.0013	47[f,g]
Triptyene-2-*t*	CF_3COOH[e]	70.0	0.348 ± 0.004	367[f,h]

[a] LiCHA is lithium cyclohexylamide; CsCHA, cesium cyclohexylamide in cyclohexylamine (CHA) solution. [b] A. Streitwieser, Jr., R. G. Lawler, and C. Perrin, *J. Am. Chem. Soc.*, **87**, 5383 (1965). [c] A. Streitwieser, Jr., and H. F. Koch, *ibid.*, **86**, 404 (1964). [d] Rate constant based on points after 98% reaction. [e] Solution contained 2% CCl_4. [f] K. C. C. Bancroft, R. W. Butt, and C. Eaborn, *Chem. Ind.* (London), 1951 (1965). [g] Reference 10 reports $k = 0.0484 \times 10^{-5}$ sec^{-1} and $k/k_{PhT} = 51$. [h] Reference 10 reports $k = 0.344 \times 10^{-5}$ sec^{-1} and $k/k_{PhT} = 362$.

Biphenylene undergoes electrophilic aromatic substitution primarily at the 2 position.[3] Tritiodeprotonation in trifluoroacetic acid media is 64–135 times faster at the 2 than at the 1 position.[4,5] Although the 2 position is indeed predicted to be somewhat the more reactive by MO theories, the difference is far greater than localization energies predict.[4] In contrast, biphenylene is readily metalated at the 1 position.[5,6] This characteristic extends to the relative kinetic acidities as well: in protodetritiation with LiCHA in cyclohexylamine at 50°, the 1 position is 79-fold more reactive than the 2 position. We have shown previously that such exchange rates of polycyclic aromatic hydrocarbons can be correlated quantitatively with a simple field-effect function.[7] This correlation applies well to biphenylene-2-*t*; a rate relative to benzene-*t* of 5.6 is predicted compared to the experimental value of 6.2. For biphenylene-1-*t* the predicted relative rate of 8.6 is much smaller than the experimental value, 490. Similarly, for benzo[*b*]biphenylene-5-*t*, the calculated relative rate for this biphenylene-1 type position, 64, is much less than the experimental value, 2150.

Electrophilic substitution in benzcyclobutene occurs primarily at the 4 position;[8] however, metalation occurs primarily at the 3, or *ortho*, position.[9] Our preliminary results with tritiodeprotonation with CsCHA in CHA at 25° indicate that the 3 position is seven times more reactive than the 4.

The ring juncture of triptycene is a site of strain. Protodetritiation in trifluoroacetic acid at 70° is 7.8 times faster at the 2 position than at the 1.[10] Toward CsCHA in CHA at 25° the 1 position is the more reactive by a factor of 7.5.

Although *ad hoc* explanations could probably be applied to individual results in this series, these re-

---

(1) W. H. Mills and I. G. Nixon, *J. Chem. Soc.*, 2510 (1930).

(2) K. C. C. Bancroft, R. W. Bott, and C. Eaborn, *ibid.*, 4806 (1964).

(3) W. Baker and J. F. W. McOmie in "Non-Benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959; M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press Inc., New York, N. Y., 1967.

(4) A. Streitwieser, Jr., and I. Schwager, *J. Am. Chem. Soc.*, **85**, 2855 (1963).

(5) J. M. Blatchly and R. Taylor, *J. Chem. Soc.*, 4641 (1964).

(6) W. Baker, A. J. Boulton, C. R. Harrison, and J. F. W. McOmie, *Proc. Chem. Soc.*, 414 (1964).

(7) A. Streitwieser, Jr., and R. G. Lawler, *J. Am. Chem. Soc.*, **85**, 2854 (1963); **87**, 5388 (1965).

(8) J. B. F. Lloyd and P. A. Ongley, *Tetrahedron*, **21**, 245 (1965).

(9) R. A. Finnegan, *J. Org. Chem.*, **30**, 1333 (1965).

(10) Results substantially in agreement with ours were reported recently by R. Taylor, G. J. Wright, and A. J. Holmes, *J. Chem. Soc., Sect. B*, 780 (1967). Note that in the experimental section of this paper the triptycene positions are apparently mislabeled with reference to the rate constants.

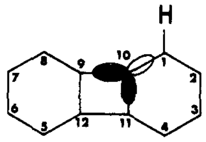

Figure 1. Biphenylene. Shaded orbitals have increased p character; hence, unshaded orbital has increased s character.

sults as well as numerous other qualitative observations in the literature obey the following generalization: *aryl positions adjacent to a fused strained ring have enhanced acidity and reduced reactivity toward electrophilic substitution.* Our interpretation follows from Figure 1. The atomic orbitals of the fused aryl carbon used to construct the strained ring have higher p character. Hence, the remaining orbital has higher s character. The *o*-carbon is thus bound to an orbital of higher electronegativity and the observed properties follow.

Acknowledgment. This research was supported in part by grants from the National Institutes of Health, Air Force Office of Scientific Research, and Petroleum Research Fund.

(11) National Institutes of Health Predoctoral Fellow, 1964–1966.

(12) National Science Foundation Predoctoral Fellow, 1960–1963; Eastman Kodak Science Award in Chemistry, 1962–1963.

Andrew Streitwieser, Jr., G. R. Ziegler[11]
P. C. Mowery, A. Lewis, R. G. Lawler[12]
Department of Chemistry, University of California
Berkeley, California 94720
Received December 16, 1967

The Crystal and Molecular Structure of the 1:1 Adduct of Antimony(V) Fluoride and Sulfur Dioxide[1]

Sir:

We wish to report on the structure of crystalline $SbF_5\cdot SO_2$, a compound of increasing interest because of the use of antimony pentafluoride solutions in liquid sulfur dioxide to produce carbonium ions.[2]

The compound was prepared by the method of Aynsley[3] who reported a melting point of 57°. The crude product was purified by sublimation to give a colorless solid, mp 66–72°, which was recrystallized from liquid SO_2, mp 62–67°. *Anal.*[4] Calcd for $SbF_5\cdot SO_2$: Sb, 43.2; S, 11.4; F, 33.8. Found: Sb, 40.73; S, 10.58; F, 32.19. The infrared spectra of the sublimed and recrystallized materials, obtained on the powdered solid between AgCl plates, were identical, showing bands at 1625 (w), 1323 (s), 1145 (sh w), 1100 (m), 696 (s), and 480 cm^{-1} (w).[5]

The structure was determined by single-crystal X-ray methods. $SbF_5\cdot SO_2$ crystallizes in the $P2_1/c$ space group with unit cell dimensions: a = 5.84 Å; b = 10.50 Å; c = 10.54 Å; β = 109° 35′; Z = 4.

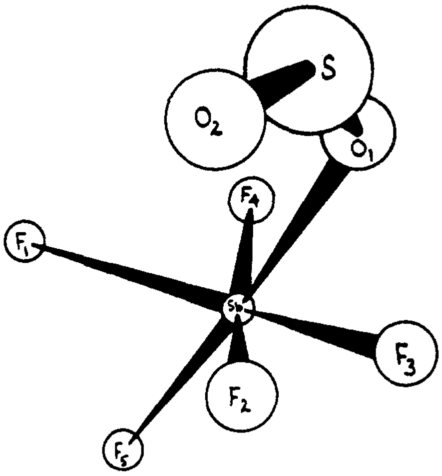

Figure 1. Isometric projection of $SbF_5\cdot SO_2$.

The 1003 independent reflections, recorded by the Weissenberg multiple-film technique, were judged visually and gave an R value[6] of 0.09 after the usual Patterson and Fourier syntheses followed by a least-squares refinement with anisotropic temperature factors.[7]

The structure so obtained is shown in Figure 1. The five fluorine atoms and O_1 outline a highly symmetrical octahedron which is elongated in the direction of the F_5–O_1 axis.

The largest standard deviation for the bond lengths, which are uncorrected for thermal rocking motion, is 0.016 Å, and those for the bond angles are commensurate. The bond lengths (Å) are: Sb–O_1, 2.13; Sb–F_1, 1.87; Sb–F_2, 1.84; Sb–F_3, 1.86; Sb–F_4, 1.84; Sb–F_5, 1.85; S–O_1, 1.45; S–O_2, 1.38. The O_1–Sb–F_5 angle is 178.2°, the F_1–Sb–F_3 angle is 170.4°, and the F_2–Sb–F_4 angle is 170.6°. Atoms F_1, F_2, F_3, and F_4 are coplanar within 0.05 Å, and the antimony atom is displaced 0.14 Å from that plane in the direction of F_5. The Sb–O_1–S angle is 138.9°. The oxygen–sulfur–oxygen angle of 119.2°, the S–O_1 bond length of 1.45 Å, and the S–O_2 bond length of 1.38 Å compare with an angle of 119.0° and a bond length of 1.43 Å found in crystalline SO_2.[8] The Sb–O_1 bond length of 2.13 Å is in good agreement with the antimony–oxygen bond length of 2.12 Å found in $SbCl_5\cdot(CH_3)_2SO_2$.[9] The shortest intermolecular contact distance is 2.86 Å which occurs between S and F_2, and S and F_5.

The ^{19}F nmr spectrum[10] at −78° in liquid SO_2 is consistent with the structure shown. Two peaks are observed, a doublet (J = 100 cps) at 105 ppm and a broad resonance at 137 ppm upfield relative to CCl_3F as an external standard. On integration the ratio was 4:1. We were not able to resolve the broad resonance, but its width was consistent with the expected quintet and the J value of 100 cps.

---

(1) Based on the dissertation submitted by J. W. Moore to the Division of Graduate Studies, Wake Forest University, in partial fulfillment of the requirements for the Master of Arts degree.

(2) (a) G. A. Olah and M. B. Comisarow, *J. Am. Chem. Soc.*, **89**, 2694 (1967), and a number of previous papers of that series; (b) M. Brookhart, F. A. L. Anet, and S. Winstein, *ibid.*, **88**, 5657 (1966); M. Brookhart, A. Diaz, and S. Winstein, *ibid.*, **88**, 3135 (1966).

(3) E. E. Aynsley, R. D. Peacock, and P. L. Robinson, *Chem. Ind.* (London), 1117 (1951).

(4) Analysis by Alfred Bernhardt, Mikroanalytisches Laboratorium, im Max-Planck-Institut für Kohlenforschung, Mülheim (Ruhr), West Germany.

(5) The spectra were obtained on a Perkin-Elmer Model 621 spectrophotometer.

(6) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

(7) W. R. Busing, K. O. Martin, and H. A. Levy, OR FLS-A Fortran Crystallographic Least-Squares Program, ORNL-TM-305, Oak Ridge National Laboratory, 1962, modified (H. W. B.) for the IBM 360-30.

(8) B. Post, R. S. Schwartz, and I. Fankuchen, *Acta Cryst.*, **5**, 372 (1952).

(9) C.-I. Brändén, A. Hansson, Y. Hermodsson, and I. Lindqvist, *Z. Krist.*, 117, 464 (1962).

(10) Obtained on a Varian A 56/60 spectrometer.