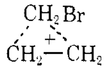
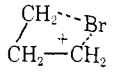
A noncommittal representation has been used for I and II. Using I for an example, either bridged (III) or edge-attached (IV) geometries are attractive. At present, there is little basis for choice and they may interconvert so rapidly that the distinction loses importance. Baird and Aboderin invoked both forms and felt that this was necessary on the basis that unequal amounts of deuterium were found on C-1 and C-2 in the 1-propyl derivatives. Their argument does not seem acceptable in view of the magnitude of kinetic isotope effects,[2] and furthermore, in our work on D_2SO_4 plus cyclopropane (the details to be published later), equal amounts of deuterium were found on C-1 and C-2.


III


IV

The three dibromopropanes were identified by gas chromatography (gc) retention times and by proton magnetic resonance (pmr) spectra of samples isolated by preparative gc. Authentic samples were used for comparison in both types of observations.[3]

The additions of Br_2 to cyclopropane is presented in texts as typifying additions to cyclopropane, and the product is given as 1,3-dibromopropane. In the light of the data in Table I, it is of interest to examine the basis for this presentation. Gustavson[4] could not separate the dibromopropanes produced. On the basis that the mixture gave both propene and cyclopropane on treatment with Zn dust, Gustavson concluded that both 1,2- and 1,3-dibromopropanes had been present.

The addition of Br_2 to cyclopropane at 25° under irradiation has been variously reported (1) to react slowly and give unidentified products[5] and (2) to produce 1,3-dibromopropane.[6] The latter report based the identification on refractive index and density, which is unsatisfactory. Curiously, Cl_2 plus cyclopropane at $-30°$ in the presence of 1% $FeCl_3$ gave over 90% 1,3-dichlorocyclopropane.

One other example of 1,2 addition to cyclopropane existed at the time of this work. It had been found that acetylation of cyclopropane produced products of 1,2 and 1,3 addition with the 1,2-addition product dominating in the ratio 2:1.[7] Recently, Hart and Schlosberg have reinvestigated this reaction and found up to 10% of the 1,1-addition product under certain conditions.[8] They have interpreted these results in terms of intermediate protonated cyclopropanes, and our interpretations parallel theirs.

One other aspect of the presentation in texts is misleading. In the addition of Br_2 to cyclopropane no catalyst is indicated, whereas in the bromination of benzene $FeBr_3$ is usually placed above the arrow, indicating that it is required. We have found that $FeBr_3$ is needed even more for the cyclopropane reaction than for the benzene reaction.[9] In a competition experiment between benzene and cyclopropane at $-12°$, using 1% $FeBr_3$ as a catalyst (introduced as Fe + Br_2) and a deficiency of Br_2, the products were entirely bromobenzene and bromopropane (from HBr + cyclopropane). It is concluded that cyclopropane is much less reactive toward Br^+ than is benzene.

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[2] The closest analogy is the effect of α-deuteration on carbonium ions where the calculated k_H/k_D for an isolated carbonium ion is 1.4 and the observed SN1 solvolysis rates average around 1.15 (A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 173).

[3] The 1,1-dibromopropane was made by treatment of α-bromobutyramide with Br_2 in aqueous alkali (C. L. Stevens, T. K. Mukerjee, and V. J. Traynelis, *J. Am. Chem. Soc.*, **78**, 2264 (1956). The other two isomers were commercially available.

[4] G. Gustavson, *J. Prakt. Chem.*, [2] **62**, 273 (1900), and earlier papers.

[5] M. S. Kharasch, M. Z. Fineman, and F. R. Mayo, *J. Am. Chem. Soc.*, **61**, 2139 (1939).

[6] R. A. Ogg, Jr., and W. J. Priest, *ibid.*, **60**, 217 (1938).

[7] H. Hart and O. E. Curtis, Jr., *ibid.*, **79**, 931 (1957); H. Hart and G. Levitt, *J. Org. Chem.*, **24**, 1267 (1959).

[8] H. Hart and R. H. Schlosberg, submitted for publication.

[9] Gustavson[4] reported that concentrated aqueous HBr catalyzed the addition of Br_2 to cyclopropane. In our hands, it was without effect.

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Anisole in Sulfuric and Fluorosulfuric Acid

Sir:

The position of protonation of anisole is of theoretical interest and practical importance in the use of anisole or similar compounds as Hammett bases. It is well established[1,2] that anisole in $HF-BF_3$ or SbF_5-FSO_3H is protonated predominately on the *p*-carbon. Ultraviolet spectral evidence has been interpreted to suggest that in aqueous H_2SO_4 anisole protonates predominately on oxygen.[3]

A recent communication[4] suggested that solvents which promote hydrogen bonding will favor protonation of anisole on oxygen, and that in concentrated sulfuric acid one may observe a change from C to O protonation. While reasonable and relevant in comparison of aqueous acids with systems such as $HF-BF_3$, the proposal unfortunately centers around an incorrect assignment to *para*-protonated anisole of the 284- and 240-mμ bands which appear in the ultraviolet spectrum of anisole in concentrated H_2SO_4. The λ_{max} 284 mμ band has been assigned by Birchall and Gillespie[1a] to *para*-protonated anisole, whereas in fact the spectrum observed in concentrated H_2SO_4 must be attributed to sulfonated anisole.

We have found the text of ref 1b on the nmr spectrum of anisole in FSO_3H to be misleading. The text and presentation of spectra indicate at room temperature a CH_3 resonance at δ = 4.8 ppm relative to external TMS, with the appearance of a new CH_2 resonance at 4.4 ppm when the sample is cooled below 0°. Examination of the published room temperature spectrum, using the published scale, indicates the CH_3 resonance at 4.4 ppm, *not at 4.8 ppm*.

We have found that the nmr spectra of anisole in FSO_3H and concentrated H_2SO_4 are substantially the

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[1] (a) T. Birchall, A. Bourns, R. Gillespie, and B. Smith, *Can. J. Chem.*, **42**, 1433 (1964); (b) T. Birchall and R. Gillespie, *ibid.*, **42**, 503 (1964).

[2] D. M. Bronwer, E. L. Mackor, and C. Maclean, *Rec. Trav. Chim.*, **85**, 109 (1966).

[3] E. M. Arnett and C. Y. Wu, *J. Am. Chem. Soc.*, **82**, 5660 (1960).

[4] A. J. Kesege and L. E. Hakka, *ibid.*, **88**, 3868 (1966).

same when the solutions are prepared and spectra run at room temperature. On cooling anisole–FSO_3H acid solutions whose room temperature spectra were identical with the published spectra ($\delta(CH_3) = 4.4$ ppm) to $-60°$, no change in the spectra could be observed.[5] Inasmuch as the CH_3 nmr resonance of *para*-protonated anisole in other solvents occurs near 4.8 ppm,[1,2] and the methyl resonances of methoxyalkyl cations in general occur between 4.8 and 5.2 ppm,[6] the published and observed nmr spectra of anisole in either FSO_3H or H_2SO_4 at room temperature are inconsistent with that expected of the *para*-protonated anisole.

The ultraviolet spectrum of anisole in 92% H_2SO_4, prepared either by adding anisole to cold 92% H_2SO_4 or by diluting anisole in 98% H_2SO_4, is in all details independent of its mode of preparation and, except for a slight blue shift ($\approx$1 mμ), identical with spectra in 98% H_2SO_4. On diluting anisole–H_2SO_4 solutions to 80% water, the 284-mμ band is transformed, with little change in molar extinction coefficient, into a typical aromatic band (λ_{max} 278 mμ), with the disappearance, or large blue shift, of the 240-mμ band. Virtually identical solvent effects may be observed in the ultraviolet spectrum of toluenesulfonic acid, λ_{max} (H_2SO_4) 271, 262, and 237 mμ; λ_{max} (H_2O) 259 mμ.

Finally, we are unable to recover anisole detectable by vpc from anisole–H_2SO_4 or –FSO_3H acid solutions after drowning on ice when the solutions are more than a minute or so old. Indeed we have found, by the simple expedient of noting the presence or absence of a cloudy solution after pouring anisole–H_2SO_4 into water, that sulfonation of anisole in 92% or greater H_2SO_4 is complete at room temperature in a matter of seconds. A high-boiling water-insoluble product may be recovered from anisole–FSO_3H. This product gives a single peak on vpc at 210° on an SE-30 column. The infrared and nmr spectra indicate this product to be almost entirely *ortho*-substituted anisole; presumably by analogy with the known reaction in $ClSO_3H$, the product is *o*-anisylsulfonyl fluoride.

In conclusion, the published nmr spectrum[1b] of anisole in FSO_3H at room temperature and the ultraviolet maxima at 284 and 240 mμ in H_2SO_4 may not be assigned to *para*-protonated anisole. On the basis of known reactions, comparison of solvent effect on ultraviolet spectra, nmr spectra, and the high water solubility of products from H_2SO_4, the species responsible for these spectra almost without doubt are anisyl sulfonation products. It has already been reported[7] that *p*-methylanisole and *p*-anisylamine have sulfonation half-lives of less than 1 min in concentrated sulfuric acid at room temperature.

Given the above conclusions, the question remains, does the absence of a new maximum at wavelengths greater than 270 mμ in the spectra of anisole in more dilute H_2SO_4 and $HClO_4$ acid preclude *para* C protonation of anisole in these systems? Kesege and Hakka[4] have assigned a *shoulder* which appears at 285 mμ in the spectrum[8] of anisole in concentrated $HClO_4$ to the *para*-protonated species. This assignment[4] is based on a predicted λ_{max} 285 mμ obtained by extrapolation of data from more highly substituted alkoxybenzenes which are C protonated.

On the other hand, Ramsey and Taft[6] have reported that the ultraviolet spectra of R_2C^+OR' ions are largely independent of whether R' is H or CH_3. Therefore, we feel O-protonated 1,4-cyclohexadienone in H_2SO_4 should be an excellent model for *para*-C-protonated anisole. The ultraviolet λ_{max} for 1,4-cyclohexadienone is not available, but the ultraviolet maximum of 6,6-dimethyl-1,4-cyclohexadienone in methanol has been reported[9] as 227 mμ. Application of the $CH_3OH \rightarrow H_2SO_4$ solvent correction obtained[10] from mesityl oxide (4-methyl-3-pentenone) of -20 kcal/mole to λ_{max} 227 mμ and correcting for alkyl substitution predicts an ultraviolet λ_{max} <270 mμ for the ultraviolet spectrum of *para*-protonated anisole. We consider this estimate of the ultraviolet absorbtion maxima of *para*-C-protonated anisole to be only a little less speculative than that of Kesege and Hakka, and suggest that currently available spectral data do not permit an unambiguous assignment of O or C protonation of anisole in aqueous acid systems at room temperature.

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[5] We have been able to reproduce the low-temperature spectra of anisole in FSO_3H by preparing the solutions at $-80°$ and running the spectra at $-60°$. Above 0° the 4.8-ppm CH_3 resonance rapidly irreversibly disappears and is replaced with a second band at 4.4 ppm. We have no trouble reproducing the anisole SbF_5–FSO_3H spectra of ref 1a.

[6] B. G. Ramsey and R. W. Taft, *J. Am. Chem. Soc.*, **88**, 3058 (1966).

[7] P. Schleyer, D. Kleinfelter, and H. Richey, Jr., *ibid.*, **85**, 479 (1963).

[8] K. Yates and H. Wai, *Can. J. Chem.*, **43**, 2131 (1965).

[9] S. Winstein and R. Baird, *J. Am. Chem. Soc.*, **85**, 567 (1963).

[10] S. Nagakura, A. Minegishi, and K. Stanfield, *ibid.*, **79**, 1033 (1957).

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Stereochemistry of Asymmetric Silicon. The Silicon–Sulfur Bond

Sir:

General interest in the chemistry of the silicon–sulfur bond, coupled with the great lack of mechanistic information concerning reactions of this bond[1] plus our previous studies of the dynamic stereochemistry of the silicon–oxygen bond,[2] have made it important to study the stereochemistry of the silicon–sulfur bond.

We wish to report: (a) the first syntheses of optically active R_3Si^*S compounds, in which R_3Si^* is α-naphthylphenylmethylsilyl, α-NpPhMeSi*; (b) a high degree of stereospecificity for reactions of the silicon–sulfur bond with various reagents; (c) some interesting changes

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[1] For previous work in the field of organosilicon sulfur chemistry see: C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, pp 333–338; V. Bažant and V. Chavalovský, "Organosilicon Compounds," Vol. 1, Academic Press Inc., New York, N. Y., 1965, pp 72–75; A. Haas, *Angew. Chem.*, **77**, 1066 (1965); H. J. Emeléus and M. Onyszchuk, *J. Chem. Soc.*, 604 (1958); E. W. Abel, *ibid.*, 4406 (1960); H. Gilman and G. Lichtenwalter, *J. Org. Chem.*, **25**, 1064 (1960); E. W. Abel, *J. Chem. Soc.*, 4933 (1961); L. Birkofer, A. Ritter, and H. Goller, *Ber.*, **96**, 3289 (1963); E. W. Abel, D. A. Armitage, and R. P. Bush, *J. Chem. Soc.*, 2455 (1964); E. W. Abel, D. A. Armitage, and R. P. Bush, *ibid.*, 3045 (1965); E. W. Abel, D. A. Armitage, and R. P. Bush, *ibid.*, 7098 (1965); K. A. Hooton and A. L. Allred, *Inorg. Chem.*, **4**, 671 (1965); E. W. Abel, D. A. Armitage, and D. B. Brady, *J. Organometal. Chem.* (Amsterdam), **5**, 130 (1966); M. Rimpler, *Ber.*, **99**, 1523 (1966); M. Rimpler, *ibid.*, **99**, 1528 (1966).

[2] (a) L. H. Sommer, C. L. Frye, and G. A. Parker, *J. Am. Chem. Soc.*, **86**, 3276 (1964); (b) L. H. Sommer, G. A. Parker, and C. L. Frye, *ibid.*, **86**, 3280 (1964).