this represents the greater part of the stabilization conventionally attributed to π-electron delocalization.

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RELATIVE REACTIVITIES OF TOLUENE, TOLUENE-α,α,α-d_3 AND TOLUENE-α-t IN ELECTROPHILIC NITRATION, MERCURATION AND BROMINATION[1]

Sir:

We have found that secondary isotope effects on the rate of nuclear aromatic nitration, mercuration and bromination due to isotopic substitution for hydrogen in the methyl group are 3% per deuterium atom or less. The larger (4–30% per deuterium) secondary isotope effects previously observed in solvolysis have been interpreted in terms of hyperconjugation in the transition state.[2] Therefore either hyperconjugation is relatively less important in these aromatic substitutions than in the solvolyses (including p-$\mathrm{CH_3{}^*C_6H_4CHClCH_3}$ in acetic acid at 50°) or the reported p-methyl isotope effects in solvolysis are not measuring hyperconjugation. In view of the extreme importance of other kinds of resonance in aromatic substitution (*e.g.*, relative rates of about $10^{18}:10^{9}:1$ for bromination of aniline, anisole and benzene[3]) it is unexpected that hyperconjugation should be so minor. Therefore we favor the latter interpretation.

Summarizing our experimental results: Toluene-α,α,α-d_3 (2.7 D) and toluene-α-t were prepared by reduction of α,α,α-trichlorotoluene with zinc and acetic acid-d or -t.[4] The molar activity of toluene-α-t recovered after 92% reaction with nitronium ion (0.5 M toluene plus 10 M nitric acid containing 20% water by volume) at 25° was 0.86 ± 0.77% higher than that of the starting material (scintillation counting) corresponding to an isotope effect of 1.003 ± 0.003 for k_H/k_T or 1.002 ± 0.002 for k_H/k_D per deuterium atom. There was no exchange of methyl hydrogens under these nitration conditions, since the nitrotoluenes produced had the same molar activity as the starting material within 2.8 ± 3.5% (ionization chamber counting).

Mercuration of toluene-α,α,α-d_3 by Hg^{++} (0.2 M toluene plus 0.05 M mercuric acetate in acetic acid solution containing 0.25 M water and 0.50 M perchloric acid) at 25° gave an isotope effect of 1.00 ± 0.03 per deuterium (determined by direct rate comparison rather than by competition experiment). Under mercuration conditions, toluene-α-t did exchange tritium slowly with the solvent, but the exchange reached less than 5% completion during the time of the mercuration kinetics.

In bromination of toluene-α-t by Br_2 (0.05 M reactants in 85% acetic acid–15% water solution) at 25° the molar activity of toluene recovered after 81% reaction showed a 7.7 ± 1.4% increase, corresponding to an isotope effect of 1.046 ± 0.009 for k_H/k_T or 1.03 ± 0.01 for k_H/k_D per deuterium atom. Bromotoluenes from complete bromination had the same molar activity as the toluene within experimental error (± 3%).

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[1] The bromination work was supported by the Office of Naval Research under Contract No. N5ori-07838 (*cf.* T. E. C. K., Ph.D. thesis, M. I. T., Sept., 1956, for complete experimental data) and subsequent mercuration and nitration work (by A. J. K.) by the Atomic Energy Commission under Contract No. AT(30-1)-905. Reproduction is permitted for any purpose of the United States Government.

[2] E. S. Lewis and C. E. Boozer, THIS JOURNAL, **74**, 6306 (1952); **76**, 791, 794 (1954); V. J. Shiner, Jr., *ibid.*, **75**, 2925 (1953); **76**, 1603 (1954); **78**, 2653 (1956); E. S. Lewis and G. M. Coppinger, *ibid.*, **76**, 4495 (1954); E. S. Lewis and R. R. Johnson, Abstracts of Papers presented at 130th Meeting of the American Chemical Soc., Atlantic City, New Jersey, Sept. 16 to 21, 1956, p. 20-O; A. Streitweiser, R. H. Jagow and S. Suzuki, THIS JOURNAL, **77**, 6713 (1955).

[3] P. W. Robertson, P. B. D. de la Mare and B. E. Swedlund, *J. Chem. Soc.*, 782 (1953).

[4] R. Renaud and L. C. Leitch, *Can. J. Chem.*, **34**, 98 (1956).

syn-7-NORBORNENYL TOLUENESULFONATE[1]

Sir:

As reported recently,[2] *anti*-7-norbornenyl p-toluenesulfonate (IV) is more reactive than the related 7-norbornyl derivative (VI) in acetolysis by a factor of 10^{11}, the anchimerically assisted ionization leading to cation (VII). We now report the preparation of the previously unavailable isomeric *syn*-7-norbornenol (III) and the novel solvolytic behavior of its toluenesulfonate (V).

From opening of bicycloheptene oxide (I) with hydrogen bromide, there is obtained predominantly the Wagner–Meerwein rearranged bromohydrin (II), m.p. 75–76°. By the action of potassium t-butoxide in benzene on the toluenesulfonate of the bromohydrin (II), there is obtained *syn*-7-norbornenyl toluenesulfonate (V), m.p. 67–68°, in *ca.* 80% yield. Hydrogenation of this material leads to the known 7-norbornyl derivative (VI). Analogous treatment of the tetrahydropyranyl derivative of the bromohydrin II with potassium t-butoxide and hydrolysis led to *syn*-7-norbornenol (III), m.p. of phenylurethan 125–126°, m.p. of p-toluenesulfonate 67–68°.

First order rate constants of acetolysis of the *syn*-toluenesulfonate (V) are $(1.17 \pm 0.02) \times 10^{-6}$ sec.$^{-1}$ at 100.0° and $(1.28 \pm 0.01) \times 10^{-5}$ sec.$^{-1}$ at 122.2°, leading to an extrapolated value of 2.6×10^{-11} sec.$^{-1}$ at 25°. While the *syn*-material (V) is slower than its *anti*-isomer (IV) by a factor of 10^7, it is nevertheless anchimerically accelerated, since it is more reactive than the 7-norbornyl ester (VI) by a factor of 10^4. The source of the anchimeric assistance is clear from the nature of the solvolysis product from (V).

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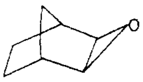
[1] (a) Research sponsored by the Office of Ordnance Research, U. S. Army; (b) supported in part by the Petroleum Research Fund of the American Chemical Society.

[2] (a) S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, THIS JOURNAL, **77**, 4183 (1955); (b) S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956); (c) C. J. Norton, Thesis, Harvard University, 1955.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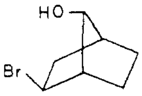

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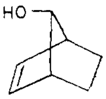

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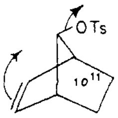

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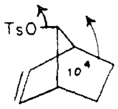

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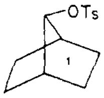

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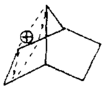
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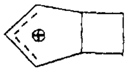
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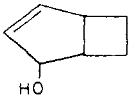

IX

Hydrolysis of the *syn*-toluenesulfonate (V) with aqueous 0.2 N sodium bicarbonate at 100° led in *ca.* 90% yield to an unsaturated liquid alcohol (A), whose crude phenylurethan had m.p. 115–118° and 118.6–119.4° after several recrystallizations. The phenylurethan analyzed correctly for that of an alcohol $C_7H_{10}O$. Quantitative hydrogenation of alcohol (A) led to a saturated alcohol (B), m.p. of phenylurethan 113–114°, analyzing correctly for the derivative of an alcohol $C_7H_{12}O$.

In its infrared spectrum alcohol (A) did not display the band at 14.0–14.2μ characteristic of the norbornenols. Instead it displayed strong bands at 12.7 and 13.6μ which disappeared on hydrogenation. As shown by m.p. and mixed m.p., the phenylurethan of alcohol (A) does not correspond to any norbornenol, all the possible 1-, 2-, or 7-isomers now being known.

On the expectation that the new alcohol (A) consisted of one or a mixture of both of the diastereomeric 2-bicyclo[3.2.0]hepten-4-ols (IX), some of this alcohol mixture was prepared by oxidation of the parent hydrocarbon,[3] bicyclo-[3.2.0]heptene-2, with selenium dioxide in acetic anhydride. The synthetic alcohol displayed the strong bands at 12.7 and 13.6 μ in the infrared spectrum. Further, it gave rise to a phenylurethan in 88% yield, m.p. 113–115.8° of the crude material, m.p. 118.2–119.4° after several recrystallizations, mixed m.p. with the phenylurethan of alcohol (A), 118.6–119.2°. It is clear that *syn*-7-norbornenyl toluenesulfonate (V) hydrolyzes to 2-bicyclo[3.2.0]heptenol-4 (IX) of still unassigned configuration.

Ionization of *syn*-7-norbornenyl toluenesulfonate (V) evidently derives substantial assistance from methylene participation, the allylic cation (VIII) being formed. Allylic resonance stabilization outweighs increase in strain associated with ring contraction, so that substantial decrease in transition state free energy results.

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[3] A. T. Blomquist and J. Kwiatek, THIS JOURNAL, **73**, 2098 (1951).

BOOK REVIEWS

Nouveau Traité de Chimie Minérale. Edited by PAUL PASCAL, Membre de l'Institut, Professeur honoraire à la Sorbonne. Tome I. **Généralites—Air—Eau—Hydrogène—Deutérium—Tritium—Hélium et Gaz Inertes.** By G. BOUISSIÈRES, M. HAISSINSKY, G. PANNETIER, P. PASCAL and R. VIALLARD. Masson et Cie, Editeurs, Libraires de l'Académie de Médecine, 120 Boulevard Saint-Germain, Paris 6, France. 1956. xii + 1101 pp. 18.5 × 25.5 cm. Price, Broché 7,500 fr.; Cartonné toile 8,400 fr.

A nineteen volume comprehensive treatise on inorganic chemistry, edited by Professor Pascal, is now being published. This series has been planned to present inorganic chemistry in a manner more consonant with the currently accepted physical theories than was possible when its predecessor was published in 1930. When complete, it should serve as the standard French language reference book on the subject.

The first volume apparently went to press late in 1954. Approximately one third of it is a survey of inorganic and physical chemistry written by Professor Pascal. The emphasis is upon bonding types, the structure of chemical entities and the observable states of matter. The approach is descriptive; the presentation is suitable for an advanced undergraduate survey course in inorganic chemistry. Where obviously applicable the terminology and results of quantum mechanics are used as unifying principles in the explanations. However an extended discussion of each subject, written in the same manner as that employed in the previous treatise, remains.

The volume also contains detailed articles about air, water and hydrogen (Pascal); deuterium and tritium (Viallard); and the inert gases (Pannetier) In keeping with the traditional pattern of the work, the literature is collated and recorded. The interpretation of the original author is usually presented. The coverage of physical properties, natural occurrence, chemical reactions and analysis is comprehensive The bibliographical references are extensive and well keyed into the text. A limited subject index is included.

An effort has been made to bring up to date the subjects covered in the earlier work. Most of the information on the isotopes of hydrogen and much of that on liquid helium is new. In general, however, a historical recitation is given of the research in each field. In many sections the work done before 1930 appears to dominate the discussion. As a source book citing the literature in the fields covered, the volume will prove valuable to the chemist who prefers to have his codified reference material in French.

Unfortunately, the book suffers from the common defect of most treatises. The sheer bulk of material mentioned along with the limitations of space preclude either a unified presentation or a critical evaluation. In the opinion of the reviewer, the extensive coverage of material available in