

this represents the greater part of the stabilization conventionally attributed to  $\pi$ -electron delocalization.

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**RELATIVE REACTIVITIES OF TOLUENE, TOLUENE- $\alpha,\alpha,\alpha$ - $d_3$  AND TOLUENE- $\alpha$ - $t$  IN ELECTROPHILIC NITRATION, MERCURATION AND BROMINATION<sup>1</sup>**

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.<sup>2</sup> Therefore either hyperconjugation is relatively less important in these aromatic substitutions than in the solvolyses (including *p*-CH<sub>3</sub>\*C<sub>6</sub>H<sub>4</sub>CHClCH<sub>3</sub> 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<sup>18</sup>:10<sup>9</sup>:1 for bromination of aniline, anisole and benzene<sup>3</sup>) it is unexpected that hyperconjugation should be so minor. Therefore we favor the latter interpretation.

Summarizing our experimental results: Toluene- $\alpha,\alpha,\alpha$ - $d_3$  (2.7 *D*) and toluene- $\alpha$ - $t$  were prepared by reduction of  $\alpha,\alpha,\alpha$ -trichlorotoluene with zinc and acetic acid-*d* or -*t*.<sup>4</sup> The molar activity of toluene- $\alpha$ - $t$  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- $\alpha,\alpha,\alpha$ - $d_3$  by Hg<sup>++</sup> (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) 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. 20-0; A. Streitwieser, 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).

1.00 ± 0.03 per deuterium (determined by direct rate comparison rather than by competition experiment). Under mercuration conditions, toluene- $\alpha$ - $t$  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- $\alpha$ - $t$  by Br<sub>2</sub> (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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***syn*-7-NORBORNENYL TOLUENESULFONATE<sup>1</sup>**

Sir:

As reported recently,<sup>2</sup> *anti*-7-norbornenyl *p*-toluenesulfonate (IV) is more reactive than the related 7-norbornyl derivative (VI) in acetolysis by a factor of 10<sup>11</sup>, 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 ± 0.02) × 10<sup>-6</sup> sec.<sup>-1</sup> at 100.0° and (1.28 ± 0.01) × 10<sup>-6</sup> sec.<sup>-1</sup> at 122.2°, leading to an extrapolated value of 2.6 × 10<sup>-11</sup> sec.<sup>-1</sup> at 25°. While the *syn*-material (V) is slower than its *anti*-isomer (IV) by a factor of 10<sup>7</sup>, it is nevertheless anchimerically accelerated, since it is more reactive than the 7-norbornyl ester (VI) by a factor of 10<sup>4</sup>. The source of the anchimeric assistance is clear from the nature of the solvolysis product from (V).

(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.