

The occurrence of *ca.* 10% of the inverted product **5** merits comment. Two reasonable possibilities exist for the formation of **5**. A direct displacement of tosylate ion by acetic acid with inversion of configuration at C-7 could account for the presence of **5**. Alternately, **10** could be "leaking" to the classical ion **11** which would then be partitioned between **4** and **5**. Precedent for this latter type of interconversion has been noted in the bicyclo[2.2.2]octyl system.<sup>15</sup> Experiments aimed at distinguishing between these two possibilities are in progress.

**Acknowledgment.** This investigation was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society.

(13) H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, *J. Am. Chem. Soc.*, **89**, 370 (1967).

(14) It should be noted that an unusual case of partial retention has recently been found in the solvolysis of a tertiary *p*-nitrobenzoate [H. L. Goering and S. Chang, *Tetrahedron Letters*, No. 40, 3607 (1965)].

(15) J. A. Berson and D. Willner, *J. Am. Chem. Soc.*, **86**, 609 (1964).

(16) National Science Foundation Trainee, 1965-1967.

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### Retention of Configuration in the Solvolysis of 2,3-Dideuterio-7-norbornyl *p*-Bromobenzenesulfonate

Sir:

Acetolysis and formolysis of *anti*-2,3-dideuterio-7-norbornyl *p*-bromobenzenesulfonate (**Ia**)<sup>1</sup> proceed with predominant retention of configuration. Therefore,

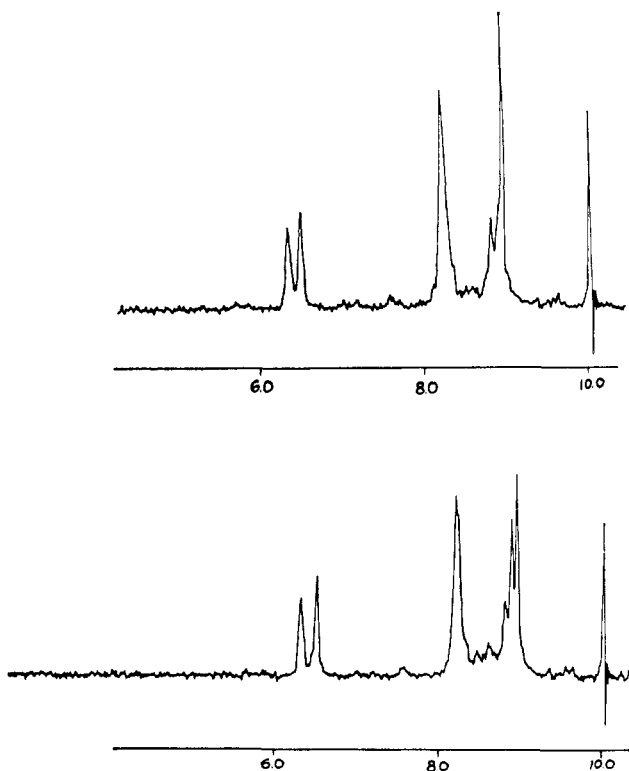


Figure 1. Nmr spectra of *anti*-2,3-dideuterionorbornan-7-ol (**Ib**) (top) and an equimolar mixture of *syn* and *anti* deuterated alcohols (bottom) in carbon tetrachloride containing tetramethylsilane.

(1) The terms *syn* and *anti* will be used to refer to the position of the deuterium atoms with respect to the oxygen function.

solvolysis cannot proceed through the free classical 7-norbornyl cation.

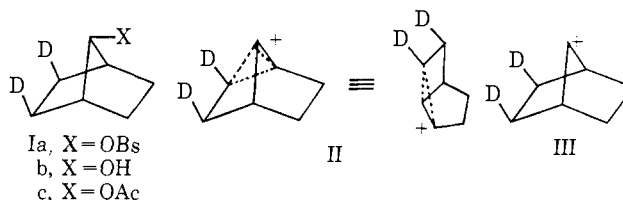
Deuterated *p*-bromobenzenesulfonate (**Ia**) was prepared from the corresponding alcohol (**Ib**) by treatment with *p*-bromobenzenesulfonyl chloride in pyridine. The alcohol was prepared by addition of deuterium gas to *anti*-7-norbornenol.<sup>2</sup> The *syn* isomer of alcohol **Ib** was prepared as an equimolar mixture with the *anti* alcohol by oxidation of *anti* alcohol with chromium trioxide in pyridine followed by lithium aluminum hydride reduction of the resulting ketone. Nuclear magnetic resonance (nmr) spectra are given in Figure 1 for *anti*-2,3-dideuterionorbornan-7-ol (**Ib**) and for an equimolar mixture of *syn* and *anti* deuterated alcohols.

Deuterated *p*-bromobenzenesulfonate **Ia** was solvolyzed for 90 min (*ca.* two half-lives) in acetic acid at 205°. The product, 7-norbornyl acetate, was isolated and purified by gas chromatography. Examination of the nmr spectrum of this acetate revealed that it consisted of 90 ± 5% *anti* acetate (**Ic**) (retention of configuration) and 10 ± 5% *syn* acetate (inversion of configuration).<sup>3</sup> The relative amounts of inversion and retention were unaffected by the presence of added sodium acetate.

Solvolysis of deuterated *p*-bromobenzenesulfonate **Ia** for 16 hr (*ca.* one half-life) in refluxing formic acid containing sodium formate gave (after saponification of the product formates) deuterated 7-norbornanol with 85 ± 5% retention of configuration.<sup>3</sup>

The predominant retention of configuration in the solvolysis of deuterated *p*-bromobenzenesulfonate **Ia** may be explained in terms of nonclassical ion **II** or in terms of classical ion **III**.

For the case of classical ion **III**, one assumes that



solvolysis proceeds through front-side collapse of an ion pair. Brown and co-workers have mentioned the possibility of front-side ion-pair collapse.<sup>4,5</sup> Examples of this have been provided by Goering and Chang in the case of 2-phenyl-2-butyl *p*-nitrobenzoate<sup>6</sup> and Shoppee and Johnston in the case of 4,4-dimethylcholestan-3-yl systems.<sup>7</sup>

The classical ion hypothesis is further supported by the fact that on the basis of the acetolysis rate correlations of Foote<sup>8</sup> and Schleyer<sup>9</sup> (a correction has been applied to Foote's correlation<sup>10</sup>) there is no evidence

(2) Alcohol **Ib** and *p*-bromobenzenesulfonate **Ia** both contained 88% of the theoretical amount of deuterium. Deuterium analysis was by J. Nemeth, Urbana, Ill.

(3) The analysis was carried out by comparison with the nmr spectra of mixtures of *syn* and *anti* alcohols or acetates of known proportion. Acetates were prepared by acetylation of the alcohols with acetic anhydride in pyridine.

(4) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *J. Am. Chem. Soc.*, **87**, 2137 (1965).

(5) H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, *ibid.*, **89**, 370 (1967).

(6) H. L. Goering and S. Chang, *Tetrahedron Letters*, 3607 (1965).

(7) C. W. Shoppee and G. A. R. Johnston, *J. Chem. Soc.*, 3261 (1961).

(8) C. S. Foote, *J. Am. Chem. Soc.*, **86**, 1853 (1964).

(9) P. von R. Schleyer, *ibid.*, **86**, 1854 (1964).

for anchimeric acceleration in the acetolysis of 7-norbornyl *p*-toluenesulfonate.

Predominant retention of configuration in the solvolysis of deuterated *p*-bromobenzenesulfonate Ia is readily explained by the postulate that nonclassical ion II is an intermediate. The corresponding undeuterated nonclassical ion was proposed in 1958 by Winstein, *et al.*, in their work on the acetolysis of 7-norbornyl *p*-bromobenzenesulfonate in order to explain the fact that the rearranged acetate formed in this solvolysis, 2-bicyclo[3.2.0]heptyl acetate, is exclusively the *trans* isomer.<sup>12</sup> The presence of some *syn*-7-norbornyl product in the present work may be explained by concurrent S<sub>N</sub>2 reaction (unlikely since added sodium acetate does not change the proportion of *syn* to *anti* acetate in the acetolysis product) or by "leakage" to classical ion III. "Leakage" to a classical ion seems reasonable since there appears to be little if any rate enhancement in acetolysis.<sup>8-10</sup> There may be some rate enhancement, though. (Acceleration by a factor of up to ten or so would not be distinguishable from the scatter in the Foote and Schleyer correlations.)

It was hoped that the results of the formolysis might provide a means of choosing between the classical and nonclassical ion interpretations. If nonclassical ions are involved, formolysis at a lower temperature (here, 100°) would be expected to give relatively more retention than does acetolysis at a higher temperature (here, 205°) on the basis of the fact that in solvolysis of *erythro*- and *threo*-3-phenyl-2-butyl *p*-toluenesulfonates the amount of retention of configuration increases from 95% to over 99% in going from acetic acid at 75° to formic acid at 25°.<sup>13</sup> On the other hand, if retention is to be explained on the basis of front-side collapse of ion pairs, formolysis at 100° would be expected to give much more inversion than does acetolysis at 205°, on the basis of the fact that Jenny and Winstein found that acetolysis of *p*-methoxyphenylethyl *p*-toluenesulfonate at 75° needed to be described in terms of ion pairs and dissociated ions while formolysis at 25° was explained in terms of dissociated ions only.<sup>14</sup> Also, Winstein, *et al.*, report this same finding for 2,4-dimethoxyphenylethyl arenesulfonates.<sup>15</sup> The experimental observations of 10 ± 5% inversion in acetic acid at 205° and 15 ± 5% inversion in formic acid at 100° if anything fit the ion-pairing explanation slightly better than they do the nonclassical ion explanation, but are clearly about midway between the extremes cited above. It is

(10) Two of the twenty compounds used by Foote in his correlation have been shown to have structures different from those accepted at the time the correlation was published.<sup>11</sup> Also, 7-norbornyl *p*-toluenesulfonate is itself used in establishing the correlation. Consequently, the least-squares line of the Foote correlation was recalculated omitting the two compounds whose structures were incorrect (case A) and omitting these two compounds and also omitting 7-norbornyl *p*-toluenesulfonate (case B). The results are: case A:  $\log k_{rel} = -0.132$  ( $\nu_{CO} = 1720$ ), correlation coefficient -0.98; case B:  $\log k_{rel} = -0.133$  ( $\nu_{CO} = 1720$ ), correlation coefficient -0.95. The observed rate for 7-norbornyl *p*-toluenesulfonate is  $\log k_{rel} = -7.00$ . The calculated rate is  $\log k_{rel} = -7.00$  (case A) and  $-7.04$  (Case B).

(11) P. von R. Schleyer, W. E. Watts, and C. Cupas, *J. Am. Chem. Soc.*, **86**, 2722 (1964).

(12) S. Winstein, F. Gadiant, E. T. Stafford, and P. E. Klinedinst, Jr., *ibid.*, **80**, 5895 (1958).

(13) D. J. Cram, *ibid.*, **74**, 2129, 2137 (1952).

(14) E. F. Jenny and S. Winstein, *Helv. Chim. Acta*, **41**, 807 (1958).

(15) S. Winstein, B. Appel, R. Baker, and A. Diaz, Special Publication No. 19, The Chemical Society, London, 1965, p 120.

therefore not possible to make a clear-cut choice between the classical and nonclassical ion interpretations at this point.

Further work on the solvolysis of 7-norbornyl *p*-bromobenzenesulfonate is in progress.

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## The Structure of Cyclooctatetraeneiron Tricarbonyl in Solution<sup>1</sup>

Sir:

We recently reported that cyclooctatetraeneiron tricarbonyl (COTFe(CO)<sub>3</sub>) in solution has a 1,3-diene-bonded structure (I) and that the nmr spectrum of the compound at -145° is that of the "frozen" structure I.<sup>2</sup> Two other groups of workers, Cotton, Davison, and Faller (CDF)<sup>3</sup> and Keller, Shoulders, and Pettit (KSP),<sup>4</sup> subsequently reached conclusions different from ours. We now show that our original interpretation is correct, and that the deductions of CDF and KSP are invalid.

That COTFe(CO)<sub>3</sub> has structure I in the crystalline state is well established<sup>5</sup> and is not in dispute. CDF<sup>3</sup> present two arguments against COTFe(CO)<sub>3</sub> having structure I in solution, and they suggest a 1,5-diene-bonded (tub) structure under these conditions.

CDF's first argument is that the infrared C-H stretching bands of COTFe(CO)<sub>3</sub> in solution are different from those found in the solid, but are similar to those of 1,5-diene-bonded (tub) COT complexes. However, the great similarity of the fingerprint region of COTFe(CO)<sub>3</sub> in the solid and in solution<sup>5,6</sup> was ignored by CDF. These spectra are presented in Figure 1, together with the spectra of COTMo(CO)<sub>3</sub><sup>7</sup> and COTW(CO)<sub>3</sub>,<sup>8</sup> two compounds which have 1,5-diene-bonded (tub) structures and which display the expected<sup>9</sup> two sharp lines in their nmr spectra ( $\tau$  4.46, 5.80 and 3.66, 5.25, respectively).

In the structurally significant fingerprint region (1600-750 cm<sup>-1</sup>), only very small differences (0.1-0.3%) in the frequencies of COTFe(CO)<sub>3</sub> are observed between the solid and solution spectra. The general

(1) (a) Research supported in part by the National Science Foundation; (b) research sponsored in part by the U. S. Army Research Office (Durham).

(2) C. G. Kreiter, A. Maasbol, F. A. L. Anet, H. D. Kaesz, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 3444 (1966).

(3) F. A. Cotton, A. Davison, and J. W. Faller, *ibid.*, **88**, 4570 (1966).

(4) C. E. Keller, B. A. Shoulders, and R. Pettit, *ibid.*, **88**, 4760 (1966).

(5) B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 2084 (1962).

(6) R. T. Bailey, E. R. Lippincott, and D. Steele, *J. Am. Chem. Soc.*, **87**, 5346 (1965).

(7) H. D. Kaesz, S. Winstein, and C. G. Kreiter, *ibid.*, **88**, 1319 (1966).

(8) This complex has recently been prepared in these laboratories by procedures similar to those used in the preparation of the molybdenum analog (A. Maasbol, unpublished work).

(9) M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Advan. Organometal. Chem.*, **3**, 1 (1965).