

FACILE CONVERSION OF VICINAL DI-METHANESULFONATES TO OLEFINS  
WITH AROMATIC ANION RADICALS<sup>1a</sup>  
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We wish to report that treatment of di-methanesulfonates (dimesylates) of vic diols with sodium anthracene or naphthalene in THF or dimethoxyethane (DME) affords a rapid and high yield conversion to the corresponding alkene. Generally, the best technique is to slowly add an approximately 0.3 M solution of the anion radical<sup>2</sup> to a degassed, stirred, solution of the dimesylate until the intense color of the anion radical persists. Quenching the excess anion radical with air or water completes the reaction and the alkene may be isolated by usual techniques. Lower temperatures give superior yields in some instances and sodium anthracene generally appears to be somewhat superior to sodium naphthalene. Inverse addition (addition of the dimesylate to the anion radical solution) often results in much poorer yield. In Table I are reported yields of alkenes from a variety of dimesylates.

With regard to cis-trans isomerism of the resulting alkene the reaction is clearly non-stereospecific, the more stable alkene predominating in close to the equilibrium ratio. (In no case could movement of the double bond from between the two former mesylate-substituted carbons be detected.) In cyclic and other biased structures, however, where only one alkene isomer is possible the reaction should be quite useful. Of note is the fact that there is apparently no steric requirement for elimination in the dimesylate, both 4-t-butyl-cis-1-trans-2-cyclohexane-diol dimesylate (I) and exo-cis-2,3-norbornanediol dimesylate (II) being readily converted to alkene in high yield.



Other techniques for conversion of vic diols to alkenes, such as reaction of the dimesylate with iodide ion,<sup>3</sup> pyrolysis of the thione carbonate,<sup>4</sup> pyrolysis of cyclic ortho esters,<sup>5</sup> and treatment of benzaldehyde acetals with butyl lithium<sup>6</sup> require either long reaction times, high temperatures, and/or formation of a cyclic derivative from the diol. The use of  $P_2I_4$  for direct conversion of diol to alkene appears restricted to benzylic or allylic diols.<sup>7</sup> The anion radical technique, of course, suffers from the disadvantage of reducing many other functional groups; e.g., carbonyl, nitro, cyano, halogen.

Several other reducing agents were tested for their ability to convert dimesylates to alkenes. Addition of cis-1,2-cyclooctanediol dimesylate (III) in THF solution to sodium in liquid ammonia afforded only 27% of cis-cyclooctene, while with sodium naphthalene at  $-35^\circ$  the yield was ca. 80%. Treatment of III with sodium trimesitylborane<sup>8</sup> gave a respectable yield (62%) of alkene (as opposed to 92% with sodium anthracene) and this reagent may merit further study. Treatment of trans-1,2-cyclooctanediol dimesylate (IV) with zinc in boiling acetic acid for 24 hrs gave no trace of cyclooctene.

Interestingly, one cannot replace the methanesulfonyl groups with toluenesulfonyl or *p*-bromobenzenesulfonyl groups; treatment of ditosylate or dibrosylate analogs of III and IV with sodium naphthalene or anthracene yields diol and some of the related epoxides. Apparently, normal S-O cleavage of the arenesulfonyl group predominates.<sup>9</sup>

The mechanism of elimination presumably involves electron transfer to one of the mesylate groups, followed by C-O cleavage as in mono-mesylates,<sup>10</sup> reduction of the alkyl radical to the carbanion,<sup>11</sup> and finally, elimination of the adjacent mesylate as methanesulfonate anion. The almost total lack of coupling of the alkyl radical with arene anion radical, a major reaction path with simple alkyl radicals,<sup>11</sup> is probably due to the large inductive effect of the  $\beta$ -methanesulfonyl group. (Garst has similarly noted a lowered yield of coupling product for the tetrahydrofurfuryl radical.)<sup>12</sup> This inductive effect is probably also responsible for the fact that 1,2-dimesylates react by electron transfer with sodium anthracene while mono-

mesylates do not.<sup>10</sup> Further evidence for this mechanism consists of the fact that certain of the dimesylates, particularly I, give poor yields of alkene on inverse addition to concentrated sodium naphthalene, yielding instead considerable amounts of epoxide and some diol. This, again is similar to the S-O cleavage path of mono-mesylates when converted to their dianions by concentrated sodium naphthalene.<sup>10</sup>

Table I

## Yields of Alkenes from 1,2-Dimesylates

dimesylate <sup>a</sup>	m.p.	anion radical	T, °C	%alkene yield <sup>b</sup>
<u>trans</u> -1,2-cyclooctanediol	89-90.5°	naphthalene	25	90
"		anthracene	25	98
<u>cis</u> -1,2-cyclooctanediol	70-71.5° <sup>c</sup>	naphthalene	25	95
"		anthracene	25	99
<u>cis</u> -1,2-cyclododecanediol	90-91.5°	naphthalene	25	84 <sup>d</sup>
"		"	-15	92 <sup>d</sup>
"		anthracene	25	78 <sup>d</sup>
<u>exo-cis</u> -2,3-norbornanediol	119-121°	naphthalene	10	74
"		"	-60	97
"		anthracene	25	92
"		"	-10	98
4-t-butyl- <u>cis</u> -1- <u>trans</u> -2-cyclohexanediol	117-8°	naphthalene	25	55
"		anthracene	25	91 <sup>e</sup>
1,2-octadecanediol	63-4°	naphthalene	25	75
"		anthracene	25	70
<u>threo</u> -2,3-octanediol <sup>f</sup>		naphthalene	40	88 <sup>g</sup>
"		anthracene	0	78 <sup>g</sup>
"		"	40	72 <sup>g</sup>
<u>trans</u> -1,2-cyclohexanediol	128-9° <sup>h</sup>	naphthalene	25	85
<u>dl</u> -2,3-butanediol	96-8°	naphthalene	25	65 <sup>i,j</sup>
<u>meso</u> -2,3-butanediol	67.5-69°	"	25	55 <sup>i,k</sup>
"		"	-50	89 <sup>k</sup>

(Notes to Table I)

<sup>a</sup>All new dimesylates gave proper C and H analyses and exhibited nmr spectra in accord with structure. All were prepared from the corresponding diols in 70-80% yield by treatment with methanesulfonyl chloride in pyridine at 0°. <sup>b</sup>Measured by gas chromatography; precision is at least + 5%. <sup>c</sup>Lit. m.p. 69-70°; T. Durst and K. C. Tin, Can. J. Chem., 48, 845 (1970). <sup>d</sup>Mixture of isomers; ca. 60% cis at lower temperatures, ca. 60% trans, otherwise. <sup>e</sup>Sodium anthracene added very slowly. <sup>f</sup>Oil, b.p. 90°/0.8 mm. <sup>g</sup>Mixture of isomers, 80-85% trans. <sup>h</sup>Lit. m.p. 136°; R. H. Wiley and H. Kraus, J. Org. Chem., 22, 994 (1957). <sup>i</sup>Actual yield probably higher. <sup>j</sup>Mixture of 2-butenes, 71% trans. <sup>k</sup>Mixture of 2-butenes, 75% trans.

#### References

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- (1b) Alfred P. Sloan Research Fellow, 1968-72.
- (2) See W. D. Closson, S. Ji, and S. Schulenberg, J. Amer. Chem. Soc., 92, 650 (1970) for details of preparation and handling of anion radical solutions.
- (3) J. K. N. Jones and J. L. Thompson, Can. J. Chem., 35, 955 (1957); L. D. Hall, L. Hough, and R. A. Pritchard, J. Chem. Soc., 1537 (1961).
- (4) E. J. Corey and J. Schulman, Tetrahedron Lett., 3655 (1968).
- (5) G. Crank and F. W. Eastwood, Austr. J. Chem., 17, 1392 (1964).
- (6) J. N. Hines, M. J. Peagram, G. H. Whitham, and M. Wright, Chem. Commun., 1593 (1968).
- (7) R. Kuhn and A. Winterstein, Helv. Chim. Acta, 11, 87 (1928); H. H. Inhoffen, K. Radscheit, U. Stache, and V. Koppe, Justus Liebigs Ann. Chem., 684, 24 (1965).
- (8) S. D. Darling, O. N. Devgan, and R. E. Cosgrove, J. Amer. Chem. Soc., 92, 696 (1970).
- (9) W. D. Closson, P. Wriede, and S. Bank, ibid., 88, 1581 (1966).
- (10) J. R. Ganson, S. Schulenberg, and W. D. Closson, Tetrahedron Lett., 4397 (1970).
- (11) J. F. Garst, J. T. Barbas, and F. E. Barton, J. Amer. Chem. Soc., 90, 7159 (1968); G. D. Sargent and G. A. Lux, ibid., 90, 7160 (1968).
- (12) J. F. Garst, Accounts Chem. Res., 4, 400 (1971).