collected and recrystallized from methanol yielding ethylamine picrate (0.52 g.), m.p. 167–169°, unchanged on mixing with an authentic sample. The original reaction mixture was evaporated to dryness under reduced pressure and the residue was recrystallized from ethyl acetate. After two recrystallizations N-ethyllutidone (0.20 g.), m.p. 160–162°, was obtained.

Anal. Calcd. for $C_9H_{13}NO$: C, 71.45; H, 8.68; N, 9.27. Found: C, 71.04; H, 8.64; N, 9.39.

Bis-2,7-ethylaminohepta-2,5-dien-4-one (IV, R = Et).—Dehydroacetic acid (5.0 g.) was dissolved in 70% aqueous ethylamine (25 ml.) and warmed on a steam bath for 30 min. On cooling, crystals precipitated and these were collected (4.0 g.), m.p. 89–90°. Recrystallization from ethanol gave pure bis-2,7-ethylaminohepta-2,5-dien-4-one as needles, m.p. 90–91°.

Acknowledgment.—The author wishes to thank Professor David Shemin for his invaluable help. This work was supported by grants from the National Institutes of Health, U. S. Public Health Service (A-1101), and National Science Foundation.

The Mechanism of the Lithium Aluminum Hydride Cleavage of Alkyl Tosylate

LLOYD J. DOLBY AND DAVID R. ROSENCRANTZ

Department of Chemistry, University of Oregon, Eugene, Oregon

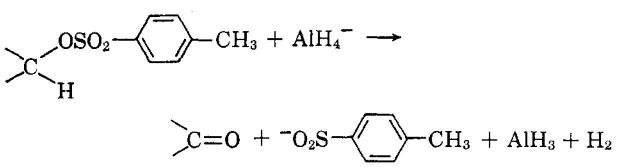
Received January 2, 1963

The cleavage of *trans*-9-decalylcarbinyl tosylate with lithium aluminum deuteride does not introduce deuterium into the *trans*-9-decalylcarbinol or the *p*-tolyl disulfide formed by reduction *p*-toluenesulfinate ion generated in the cleavage reaction. It is concluded that the cleavage reaction occurs by nucleophilic attack of aluminohydride ion on sulfonate sulfur.

A common side reaction in the lithium aluminum hydride reduction of alkyl tosylates is cleavage with regeneration of the parent alcohol.[1,2] The most likely stoichiometry for this process involves the formation of *p*-toluenesulfinate ion with the liberation of hydrogen. *p*-Toluenesulfinic acid and its reduction products have been isolated from the reaction when cleavage is the predominant course of the reaction.[1]

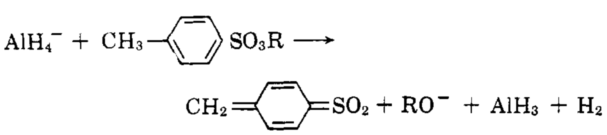
Three possible mechanisms for the cleavage reaction may be considered. The most likely is direct nucleophilic attack on sulfonate sulfur by aluminohydride ion to give an isomer of *p*-toluenesulfinic acid and alkoxide ion. Subsequent reaction with a hydride donor would liberate hydrogen to give *p*-toluenesulfinate ion. There are numerous examples of nucleophilic attack on sulfonate sulfur[3] and this mechanism requires no further comment.

A more speculative mechanism involves the base-catalyzed elimination of the elements of *p*-toluenesulfinic acid to give an intermediate carbonyl compound which would be rapidly reduced in a second step.



This type of elimination has been observed in the reaction of α-*p*-toluenesulfonyloxy ketones with alkoxides[4] and in the conversion of an α-*p*-toluenesulfonyloxylactam to an α-ketolactam with potassium *tert*-butoxide.[5]

The third possible mechanism involves a quinonoid intermediate generated by proton abstraction from the methyl group of the *p*-toluenesulfonate portion of the molecule.



This intermediate would presumably be reduced to *p*-toluenesulfinate by a hydride donor.

To test these mechanisms we have examined the products from the cleavage of an alkyl tosylate with lithium aluminum deuteride. The first mechanism predicts no deuterium incorporation in the recovered alcohol or the *p*-toluenesulfinate and its reduction products. The second mechanism requires incorporation of deuterium at the carbinol carbon atom and the third mechanism requires incorporation of deuterium into the methyl group of *p*-toluenesulfinic acid and its reduction products.

trans-9-Decalylcarbinyl tosylate was chosen as the alkyl tosylate because it is readily available and it has been shown to yield considerable cleavage product, *trans*-9-decalylcarbinol, upon lithium aluminum hydride reduction.[6,7] In the present investigation, the reduction of *trans*-9-decalylcarbinyl tosylate with lithium aluminum deuteride afforded *trans*-9-decalylcarbinol in 25% yield and *p*-tolyl disulfide in 2.5% yield. There was also a quantity of oil obtained which was undoubtedly deuterated *trans*-9-methyldecalin.[6,7] It was found that the *trans*-9-decalylcarbinol contained 0.03 atom of deuterium per molecule.[8] This evidence argues against the cleavage reaction proceeding by way of the aldehyde.

It is conceivable that part of the cleavage reaction occurs by attack of *p*-toluenethiolate ion, formed by reduction of *p*-toluenesulfinate, on sulfonate sulfur to give *p*-tolyl *p*-toluenethiolsulfonate. However, this seems unlikely because the reaction of *cis*-3-benzyloxy-*trans*-9-decalycarbinyl tosylate with benzyl mercaptide ion gives the benzyl thioether.[6]

---

(1) H. Schmid and P. Karrer, *Helv. Chim. Acta*, **32**, 1371 (1949).

(2) D. H. R. Barton and C. J. W. Brooks, *J. Chem. Soc.*, 257 (1951).

(3) For a leading reference, see J. F. Bunnett and J. Y. Bassett, Jr., *J. Org. Chem.*, **27**, 2345 (1962).

(4) A. S. Kende, *Org. Reactions*, **11**, 285 (1960).

(5) W. G. Kofron, Ph.D. thesis, University of Rochester, 1960.

(6) A. S. Hussey, H. O. Liao, and R. H. Baker, *J. Am. Chem. Soc.*, **75**, 4727 (1953).

(7) W. G. Dauben, J. B. Rogan, and E. J. Blanz, Jr., *ibid.*, **76**, 6384 (1954).

(8) Deuterium analysis were carried out by the falling drop method by Josef Nemeth, Urbana, Ill.

The details of the formation of *p*-tolyl disulfide are not clear. It must be formed from *p*-toluenesulfinate ion originating in the cleavage reaction since the reaction of lithium *p*-toluenesulfonate with lithium aluminum hydride did not give *p*-toluenethiol or *p*-tolyl disulfide under the conditions used for the reduction of *trans*-9-decalycarbinyl tosylate. It has been claimed that *p*-tolyl disulfide is a primary reaction product from the lithium aluminum hydride reduction of *p*-toluenesulfinic acid.[9] However, disulfides are readily reduced by lithium aluminum hydride[9,10] and in the present case the *p*-tolyl disulfide was probably formed by air oxidation of the corresponding thiol.

By comparing the infrared spectrum of the *p*-tolyl disulfide, obtained from the lithium aluminum deuteride reduction of *trans*-9-decalylcarbinyl tosylate, with spectra of known mixtures of *p*-tolyl disulfide-α,α'-d_2 and normal *p*-tolyl disulfide, it was found to contain less than 0.2 atom of deuterium per molecule. The analysis is complicated by the fact that monodeuterated species might be present in the sample and the authentic *p*-tolyl disulfide-α,α'-d_2 (described in the Experimental section) contained approximately 1.6 atoms of deuterium per molecule. However, the results indicate that the cleavage reaction does not proceed to the extent of 10% through the quinonoid intermediate.

The results are consistent with the lithium aluminum hydride cleavage of alkyl tosylates occurring by nucleophilic attack of aluminohydride ion on sulfonate sulfur. The evidence does not exclude the possibility of nucleophilic attack on oxygen. However, this alternative is less attractive since there seems to be no analogy for nucleophilic attack on oxygen of alkyl tosylates.

Experimental[11]

***trans*-9-Decalincarboxylic acid** was prepared by the procedure of Koch and Haaf[12] using 88% formic acid and 98% sulfuric acid as suggested by Pincock, Grigat, and Bartlett.[13]

***trans*-9-Decalylcarbinol.**—*trans*-9-Decalincarboxylic acid was reduced as described by Dauben, Tweit, and MacLean[14] to yield *trans*-9-decalylcarbinol, m.p. 76–77° (lit.[14] m.p. 77–78°).

***trans*-9-Decalylcarbinyl Tosylate.**—*trans*-9-Decalylcarbinol was converted to the tosylate, m.p. 139–141° (lit.[14] m.p. 139.7–141.7°), as previously described.[14]

Reaction of *trans*-9-Decalylcarbinyl Tosylate with Lithium Aluminum Deuteride.—To a slurry of 281 mg. of lithium aluminum deuteride in 30 ml. of *n*-butyl ether was added 1.00 g. of *trans*-9-decalylcarbinyl tosylate and the resulting mixture was heated under reflux with stirring for 14 hr. The cooled reaction mixture was hydrolyzed with water and the inorganic salts were dissolved with 6 *N* hydrochloric acid. The layers were separated and the aqueous layer was extracted four times with ethyl ether. The organic extracts were combined and washed with 5% sodium hydroxide, then water. The ether solution was dried over sodium sulfate and the ethyl ether was flash-distilled after which the *n*-butyl ether was distilled at atmospheric pressure. The residue was chromatographed on 15 g. of Woelm neutral alumina, grade I. Elution with 100 ml. of 60–90° petroleum ether gave some oil which was discarded. Elution with 40 ml. of benzene (3%)–petroleum ether yielded 10 mg. (2.6%) of *p*-tolyl disulfide, m.p. 43–44°, after sublimation (lit.[15] m.p. 46°). Elution with 100 ml. of benzene gave a trace of gum and elution with 100 ml. of ether gave 131 mg. (25%) of *trans*-9-decalylcarbinol, m.p. 76–77°. The infrared spectrum was identical with that of an authentic sample. Deuterium analysis showed 0.03 atom of deuterium per molecule.[8]

The infrared spectrum of the *p*-tolyl disulfide was identical with that of an authentic sample. The absorbancies at 1040 cm.$^{-1}$ (absent in *p*-tolyl disulfide-$\alpha,\alpha' d_2$) and 1020 cm.$^{-1}$ were compared for a series of known mixtures of *p*-tolyl disulfide and *p*-tolyl disulfide-α,α'-d_2 and 0.2 atom of deuterium per mole would have been detected.

Toluene-α-d[16] was prepared by the reaction of benzylmagnesium chloride with impure deuterium oxide. The toluene-α-d was found to contain 0.78 ± 0.04 atom of deuterium per molecule by mass spectral analysis.[17]

***p*-Toluenesulfonyl Chloride-α-d.**—Toluene-α-d was chlorosulfonated by a standard procedure.[18] From 92 g. of toluene-α-d there was obtained 30 g. (16%) of *p*-toluenesulfonyl chloride-α-d, m.p. 67–68°, after two crystallizations from petroleum ether.

***p*-Toluenethiol-α-d.**—*p*-Toluenesulfonyl chloride-α-d was reduced with zinc dust using the procedure of Adams and Marvel.[19] From 15 g. of *p*-toluenesulfonyl chloride-α-d there was obtained 3.0 g. (30%) of *p*-toluenethiol-α-d, m.p. 42–43°, after crystallization from petroleum ether and sublimation (lit.[20] m.p. 42–43°).

***p*-Tolyl disulfide-α,α'-d_2** was prepared by the bromine oxidation[21] of *p*-toluenethiol-α-d. A stirred solution of 1.0 g. of *p*-toluenethiol-α-d in 100 ml. of ether was cooled to −10° and treated with 2.0 g. of bromine. Stirring was continued for 20 min. while the bromine color was discharged after which the ether was removed under reduced pressure. The residue was crystallized from aqueous ethanol and sublimed to yield 0.65 g. (66%) of *p*-tolyl disulfide-α,α'-d_2, m.p. 43–44°. The infrared spectrum showed peaks at 2200 and 1430 cm.$^{-1}$ not present in normal *p*-tolyl disulfide and greatly diminished bands at 1450, 1380, 1210, 1105, and 1040 cm.$^{-1}$ present in *p*-tolyl disulfide.

Attempted Reduction of Lithium *p*-Toluenesulfonate with Lithium Aluminum Hydride.—A slurry of 0.706 g. of anhydrous lithium *p*-toluenesulfonate and 0.76 g. of lithium aluminum hydride in 30 ml. of *n*-butyl ether was heated under reflux for 3 days. The cooled reaction mixture was hydrolyzed with water and the inorganic salts were dissolved with 6 *N* hydrochloric acid. The layers were separated and the aqueous layer was extracted four times with ethyl ether. The organic extracts were combined and extracted with 5% sodium hydroxide solution. The ether solution was dried over sodium sulfate and distilled to a volume of 0.3 ml. Neither *p*-toluenethiol nor *p*-tolyl disulfide could be detected by thin-layer chromatography on silica gel with petroleum ether (b.p. 60–90°) as solvent. Under these conditions both *p*-toluenethiol (R_f 0.45) and *p*-tolyl disulfide (R_f 0.32) were readily determined in known samples.

The basic extracts were acidified and extracted with ether. The ether extracts were evaporated to a small volume and neither *p*-toluenethiol nor *p*-tolyl disulfide could be detected by thin-layer chromatography.

---

[9] J. Strating and H. J. Backer, *Rec. trav. chim.*, **69**, 638 (1950).

[10] R. C. Arnold, A. B. Lien, and R. M. Alm, *J. Am. Chem. Soc.*, **72**, 731 (1950).

[11] All melting points and boiling points are uncorrected; distillations were carried out using a 65-cm. modified Podbielniak tantalum spiral column. Infrared spectra were determined in carbon tetrachloride solution with a Beckman IR-7 infrared spectrophotometer.

[12] H. Koch and W. Haaf, *Ann.*, **618**, 261 (1958).

[13] R. E. Pincock, E. Grigat, and P. D. Bartlett, *J. Am. Chem. Soc.*, **81**, 6332 (1959).

[14] W. G. Dauben, R. C. Tweit and R. L. MacLean, *ibid.*, **77**, 54 (1955).

[15] R. Leuckart, *J. prakt. Chem.*, [2] **41**, 179 (1890).

[16] A. Streitweiser, Jr., D. E. Van Sickle, and W. C. Langworthy, *J. Am. Chem. Soc.*, **84**, 244 (1962), and references cited therein.

[17] We are greatly indebted to Donald F. Swinehart of this department for the mass spectral analysis.

[18] H. T. Clarke, G. S. Babcock, and T. F. Murray, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 85.

[19] R. Adams and C. S. Marvel, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 504.

[20] E. Fischer, *Ber.*, **48**, 96 (1915).

[21] J. Reilly, P. J. Drumm, and B. Daly, *Proc. Roy. Irish Acad.*, **39B**, 515 (1930). *Chem. Abstr.*, **25**, 1828 (1931).