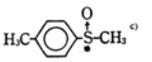
Table I. The base-catalyzed hydrogen-deuterium exchange and racemization reaction of *p*-tolyl methyl sulfoxide

Sulfoxide	Solvent	Base	Molar ratio[a]	Temp. °C	Time hr.	H–D[b] Exchange %	$[\alpha]_D$
 [c]	C_2H_5OD[d]	C_2H_5ONa	(1 : 5 : 0.5)	30—35	15	60	+152°
	C_2H_5OD[d]	C_2H_5ONa	(1 : 10 : 0.5)	105—110	15	66	+148.7°
	$(CH_3)_3COD$[e]	$(CH_3)_3COK$	(1 : 10 : 0.5)	105—110	15	20	+149°
	$(CH_3)_2SO$	$(CH_3)_3COK$	(1 : 15 : 2)	105—110	15	—	+148.2°
	$(CH_3)_2SO$	$(CH_3)_3COK$	(1 : 20 : 5)	130—135	20	not recovered[f]	

a) The molar ratio is starting sulfoxide : solvent : base.

b) The deuterium contents were analyzed by means of infrared and nuclear magnetic resonance spectroscopy.

c) $[\alpha]_D^{25}+152.3°$ (*c* 2.68, ethanol).

d) Deuterium content: 70%.

e) Deuterium content: 60%.

f) The starting sulfoxide seems to be decomposed.

The sulfoxide was recovered quantitatively, and from its melting point, ultraviolet absorption, infrared and nuclear magnetic resonance spectroscopic analyses it was found to be identical with the starting sulfoxide, except that the sulfoxide recovered was found to have incorporated a considerable amount of deuterium at the methyl group. However, the sulfoxide was found to have retained its configuration completely. The experimental conditions and the results are shown in Table I.

Although a substantial hydrogen isotopic exchange was observed to occur at the *p*-methyl group at a high temperature and with a prolonged heating, only a very small amount of hydrogen isotopic exchange at the para methyl group was observed when the reaction was performed under the relatively mild conditions in which a substantial amount of hydrogen isotopic exchange was found to take place at the other methyl group.

Moreover, the configuration around the sulfur atom of the trivalent sulfur group is retained regardless of any change in the solvent used.

These observations appear to suggest strongly that the carbanion attached to a trivalent sulfur group such as sulfoxide is stabilized by the resonance involving the 2p-orbital of carbon and the 3d-orbital of sulfur.

Experimental

(−)-Menthyl (−)-*p*-Toluenesulfinate.—The sulfinate was prepared, according to the method reported by Mislow et al.,⁶⁾ from 18.8 g. of (−)-menthol and 21 g. of *p*-toluenesulfinyl chloride⁸⁾ to give 8 g. of (−)-menthyl (−)-*p*-toluenesulfinate. (60%) M. p. 105—106°C; $[\alpha]_D^{20}$ −201° (*c* 2.0, acetone).

(+)-*p*-Tolyl Methyl Sulfoxide.⁶⁾—To a solution of (−)-menthyl (−)-*p*-toluenesulfinate (6.2 g.) in anhydrous ether (50 ml.), an ether solution of methyl magnesium iodide (prepared from 5.36 g. of methyl iodide and 1.02 g. of magnesium was added drop by drop at room temp. After it had been stirred for an hour, the reaction mixture was quenched with aqueous ammonium chloride. The ether layer was separated, washed with water, and then dried over mangesium sulfate. After the ether had been removed, the residue was cooled in an ice bath, then the precipitate was filtered to give crude (+)-*p*-tolyl methyl sulfoxide, which was recrystallized from *n*-hexane. (3.0 g., 92%) M. p. 75—76°C; $[\alpha]_D^{25}$ +152.3° (*c* 2.0, ethanol). Lit.⁶⁾ m. p. 73—74°C; $[\alpha]_D^{25}$+145.5° (*c* 2.0, acetone).

The Base-catalyzed Hydrogen-deuterium Exchange and Racemization Reaction of (+)-*p*-Tolyl Methyl Sulfoxide.—The H–D exchange and racemization reaction of the sulfoxide was performed using both C_2H_5OD and *t*-BuOD as solvents. The bases used were sodium ethoxide and potassium *t*-butoxide. Ethanol-*O-d* and *t*-butanol-*O-d* were prepared from the corresponding alkoxides with deuterium oxide.⁷⁾ The deuterium contents were determined by means of infrared and NMR studies. The D content was about 70%. A typical run was as follows: optically active (+)-*p*-tolyl methyl sulfoxide (0.3 g.) and sodium ethoxide (0.052 g.) were dissolved in ethanol-*O-d* (0.46 g.) and sealed in a glass ampoule. The ampoule was then heated in an oil bath at 105—110°C. After it had been heated for 15 hr., the reaction mixture was evaporated and the sulfoxide was recovered by extracting it with ether. (0.2 g., m. p. 75—76°C from *n*-hexane.) The optical activity of the recovered sulfoxide was checked by using a polarimeter and found to be $[\alpha]_D^{25}$ +148.7° (*c* 2.68, ethanol). The deuterium content of the methyl group attached to the sulfoxide was determined by NMR spectra.

Found: 60—66% (τ=7.27 singlet.).

When DMSO was used as a solvent, the racemization reaction of the sulfoxide was carried out with only one base, namely, potassium-*t*-butoxide.

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8) "Organic Syntheses," Coll. Vol. 4, 937 (1963).