



while the tolyl radical intermediate should abstract the  $\alpha$ -hydrogen of the alcoholic solvent. The maximum number of deuterium atoms incorporated into toluene was found to be 6 in the reactions run in alcoholic solvents having  $\alpha$ -D, while the maximum number of deuterium atoms incorporated was 5 in the product obtained from the solvents having  $\alpha$ -H (Table 2). This observation, along with the

TABLE 2. Deuterium isotope distributions in toluene.<sup>a</sup>

Run	<sup>2</sup> H <sub>0</sub>	<sup>2</sup> H <sub>1</sub>	<sup>2</sup> H <sub>2</sub>	<sup>2</sup> H <sub>3</sub>	<sup>2</sup> H <sub>4</sub>	<sup>2</sup> H <sub>5</sub>	<sup>2</sup> H <sub>6</sub>
2	9.3	20.7	33.9	22.8	9.7	3.6	0
3	7.9	15.1	26.9	27.3	18.0	2.6	2.2
5	7.4	21.3	38.5	23.2	7.9	1.5	0
6	1.7	3.1	13.8	27.8	33.2	10.2	10.2

<sup>a</sup> Determined by mass spectral analysis of the molecular ion peaks on a Hewlett-Packard g.c./m.s. Data System, Model 5982-A, corrected for the amounts of natural abundances of  $M + 1$  and  $M + 2$  ions, and expressed as percentages.

overall pattern of the deuterium distribution in toluene, clearly indicates that the  $\alpha$ -hydrogen of the solvent alcohol is abstracted by the intermediate to give toluene, and that the intermediate is most likely to be the *p*-tolyl radical species rather than the corresponding anion.

The multiple incorporation of the deuterium label into the products from the exchangeable positions of the alcoholic solvents has been determined to be a result of base-catalysed hydrogen exchange taking place primarily with the sulphonium salt. Careful n.m.r. and mass spectral analyses of the recovered tri-*p*-tolylsulphonium salt as well as of the di-*p*-tolyl sulphide product have shown relatively slow exchange at the two *ortho*-positions with respect to the sulphur substituents, and faster exchange at the methyl site. The regiospecific exchange at the *ortho*-position is also corroborated by the similar analyses performed on the triphenylsulphonium bromide system.<sup>5</sup> The site-specific *ortho*-hydrogen exchange in the triarylsulphonium salts under basic conditions could best be explained in terms of the dipole stabilization of the corresponding carbanionic species.<sup>6</sup>

The exact mechanism of the radical formation in these reactions is not yet clear. It is possible that the radical intermediate is generated either from electron-transfer processes between the sulphonium salt and the alkoxide nucleophile or from the initial formation of a sulphurane species,<sup>7</sup> followed by homolytic cleavage of the C-S bond.

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