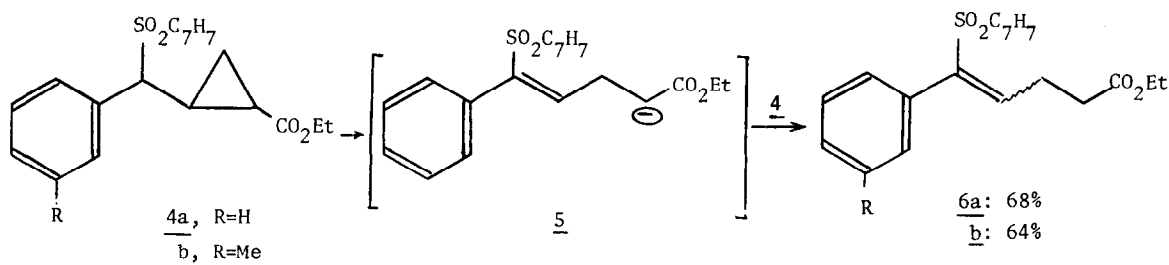




Under changed reaction conditions, a catalytic amount of lithium diisopropylamide (LDA) added to compounds 4a,b in tetrahydrofuran (THF) and hexamethylphosphoramide (HMPA)<sup>8</sup> was sufficient to effect nucleophilic ring fission<sup>9</sup> to the stereohomogeneous vinylic *p*-tolylsulfonyl derivatives (6): the initially formed anion 5 serves as the base for further deprotonation of the  $\alpha$ -sulfonylmethine group in 4. Use of excess of LDA<sup>10</sup> converted 4a,b into dienates 3a,b respectively, as the sole isolated products (64%). The intermediacy of the vinylic sulfone (6) in the above transformation was emphasized by an independent conversion of 6b into 3b (67%) under similar conditions.

Although ring cleavage and elimination of the sulfur group should occur by lithiation at several sites, the addition of methyl iodide to the above<sup>10</sup> reaction mixture containing 4a,b resulted in a stereo- and regioselective alkylative elimination to give (E,Z)-dienates 7a,b respectively (Table).<sup>7,11</sup> These results can be rationalized by the conversion of 4 to the dianion 9,<sup>12</sup> in equilibrium with 10, which is alkylated (11) in a diastereoselective manner with subsequent elimination of the nucleofugal group from an antiperiplanar conformation. We found



that alkylation can be effected by addition of MeI even after the TLC of a sample of the reaction mixture has indicated that dienate 3 has been already formed.<sup>13</sup> Formation of a vinyl anion ( $\text{Ar}-\bar{\text{C}}=\text{CH}=\text{CH}-\text{CO}_2\text{R}$ ) prior to alkylation is however not likely in view of its expected low stability in the given conditions<sup>13</sup> and the remote possibility that elimination of the sulfinate group would occur from the metalated site in 10. It is assumed therefore that the transformation 10  $\rightarrow$  3 takes place during quenching, when the protonation of the localized  $\alpha$ -sulfonyl anion may precede the protonation of the enolate anion. Use of higher homologous alkyl halides, resulted also in the formation of alkylated (E,Z)-dienates (7c-f) along with 2,5-dialkylated (E,Z)-dienates (8c-f). The latter were formed in amounts increasing with the length of the alkyl side chain. As shown in the Table, the relative yields of dialkylated products could be diminished by use of alkyl bromides instead of iodides for alkylation.

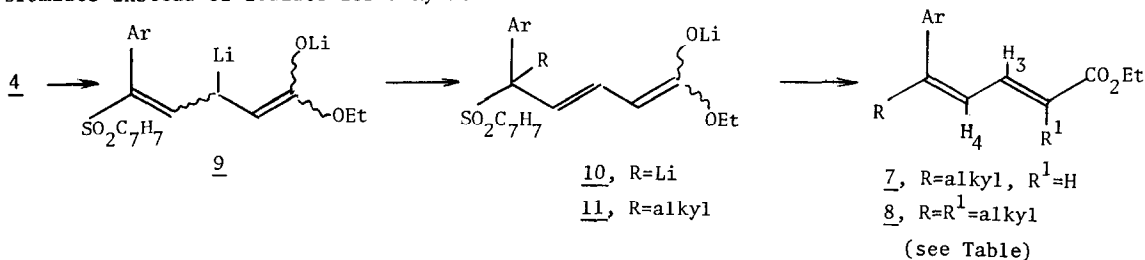


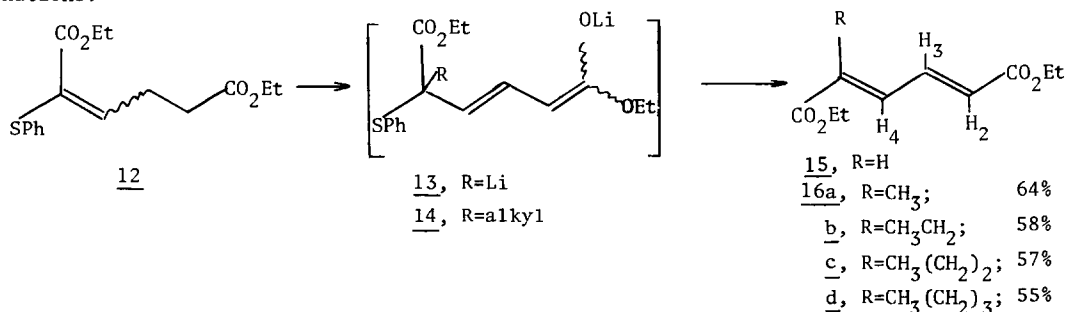
Table. Alkylative Eliminations (4 → 7 + 8)<sup>a</sup>

Entry	Alkyl halide	Compounds	<u>7</u> : <u>8</u> <sup>b</sup>	Total yield (%)
1	CH <sub>3</sub> I	<u>7a</u> , Ar=Ph	100:0	62
2	CH <sub>3</sub> I	<u>7b</u> , Ar= <u>m</u> -MeC <sub>6</sub> H <sub>4</sub>	100:0	76
3	CH <sub>3</sub> CH <sub>2</sub> I	<u>7c</u> , <u>8c</u> , Ar=Ph	72:28	58
4	CH <sub>3</sub> CH <sub>2</sub> I	<u>7d</u> , <u>8d</u> , Ar= <u>m</u> -MeC <sub>6</sub> H <sub>4</sub>	74:26	70
5	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> I	<u>7e</u> , <u>8e</u> , Ar=Ph	66:34	61
6	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> Br	<u>7e</u> , <u>8e</u>	85:15	52
7	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> I	<u>7f</u> , <u>8f</u> , Ar=Ph	58:42	61
8	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> Br	<u>7f</u> , <u>8f</u>	69:31	51

<sup>a</sup>The reaction mixture,<sup>10</sup> prepared at -78°C, was warmed to 0°C (for entries 1, 3,5,6,7,8) or -40°C (entries 2,4). The alkyl halide (fourfold excess) was added after 10 min and the reaction was continued for 20 min (entries 6,8) or 30-60 min in other cases (TLC). <sup>b</sup>Ratio and stereochemistry<sup>14</sup> were determined from <sup>1</sup>H NMR data; e.g. 7a (inter alia,  $\delta$ , CDCl<sub>3</sub>): 5.96 (H<sub>2</sub>, d, J=15 Hz), 6.55 (H<sub>4</sub>, d, J=11 Hz), 7.75 (H<sub>3</sub>, dd, J=11,15 Hz). <sup>1</sup>H NMR of 8c: 6.57 (H<sub>4</sub>, d, J=11 Hz), 7.60 (H<sub>3</sub>, d, J=11 Hz).

When cyclopropanecarboxylate 2 or its ring fission product (12)<sup>5</sup> were submitted to the action of LDA, only a very small amount of the(E,E)-2,4-hexadienoate (15) was isolated. On the other hand, the addition of an alkyl iodide to the reaction mixture containing 12 and LDA,<sup>15</sup> resulted in an alkylative elimination to give (E,E)-5-alkyl-2,4-hexadienoates 16a-d<sup>7</sup> as the sole isolated products, thus providing a simple method for the preparation of stereoselectively alkylated (E,E)-muconates.<sup>16,17</sup> Obviously, the elimination proceeds more readily after alkylation than in the presence of the delocalized  $\alpha$ -phenylthioanion in 13.

We are continuing to investigate the generality of this approach for other alkylative eliminations.



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References and Notes

1. See e.g., W.L. Parker and R.B. Woodward, J.Org.Chem., **34**, 3085 (1969).
2. For references see P.D. Magnus, Tetrahedron, **33**, 2019 (1977); B.M. Trost, Chem.Rev., **78**, 363 (1978).
3. See J. Martel and C. Huynh, Bull.Soc.Chim.France, 985 (1967); M. Julia and A. Guy-Rouault, ibid., 1411 (1967); F.M. Hauser and R.P. Rhee, J.Org.Chem., **43**, 178 (1978); J. Wildeman, P.C. Borgen, H. Plum, P.H.F.M. Rouwette and A.M. van Leusen, Tetrahedron Lett., 2213 (1978).
4. For restructuring the reactivity of allylic sulfones with Pd(0) catalyst see B.M. Trost, N.R. Schmuff and M.J. Miller, J.Am.Chem.Soc., **102**, 5979 (1980).
5. E. Ghera and Y. Ben-David, Tetrahedron Lett., 4603 (1979).
6. For similarly patterned and defined reactions see R.D. Little, and J.R. Dawson, Tetrahedron Lett., 2609 (1980).
7. All reported compounds gave analytical and spectral data consistent with the assigned structure and stereochemistry.
8. Separately prepared LDA (0.1 equiv) in THF was added to the compound (1 equiv) in THF-HMPA (10:1) at  $-100^{\circ}\text{C}$ . The reaction was quenched after 10 min ( $\text{NH}_4\text{Cl}$ ) and the product was isolated by chromatography.
9. See C.J.M. Sterling, Chem.Rev., **78**, 517 (1978), for references on ring fission of activated cyclopropanes induced by adjacent carbanions.
10. The compound (4a,b, 1 equiv) in THF-HMPA (10:1) was added at  $-78^{\circ}\text{C}$  to the LDA solution (3 equiv) in THF, and the mixture was stirred for 30 min at  $-78^{\circ}\text{C}$ , quenched ( $\text{NH}_4\text{Cl}$ ), and the product was chromatographically isolated.
11. Evidence for regioselective alkylation was obtained by oxidative cleavage ( $\text{OsO}_4\text{-NaIO}_4$ ) of 7 to the corresponding aryl alkyl ketones.
12. On allylic lithiation of vinyl sulfones see: J.J. Eisch and J.E. Galle, J.Org.Chem., **44**, 3279 (1980).
13. Compound 7a was obtained also by addition of MeI to the reaction mixture after it was kept at  $10^{\circ}\text{C}$  for 1 hr (lower yield).
14. See G. Pattenden and B.C.L. Weedon, J.Chem.Soc.(C), 1997 (1968) for an extensive study of  $^1\text{H}$  NMR spectra of stereoisomeric 5-aryl-2,4-pentadienoates. To our knowledge,  $^1\text{H}$  NMR spectra of 5-alkyl-5-aryl-2,4-pentadienoates have not been previously reported.
15. To compound 12 (1 equiv in THF-HMPA 10:1) was added successively: LDA (1.1 equiv), alkyl iodide (4 equiv, after 10 min) and again LDA (1.1 equiv, after additional 10 min). Reaction temperature:  $-78^{\circ}\text{C}$  for alkylation with MeI and  $-20^{\circ}\text{C}$  for other alkyl iodides.
16. For other methods see (a) P.L. Stotter, S.A. Roman and C.L. Edwards, Tetrahedron Lett., 4071 (1972); (b) H.D. Scharf and Y. Mattay, Liebigs Ann.Chem., 772 (1977).
17.  $^1\text{H}$  NMR data of 16a ( $\delta$ ,  $\text{CDCl}_3$ ): 6.14 ( $\text{H}_2$ , d,  $J=14$  Hz), 7.36 ( $\text{H}_4$ , d,  $J=11$  Hz), 7.56 ( $\text{H}_3$ , dd,  $J=11, 14$  Hz).

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