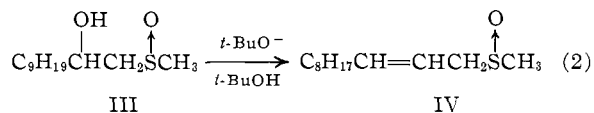




1-methylsulfinyl-2-undecene (IV), b.p. 131° (0.2 mm.). *Anal.* Calcd. for C<sub>12</sub>H<sub>24</sub>OS: C, 66.5; H, 11.2; S, 14.8. Found: C, 66.2; H, 11.3; S, 14.4. Neither 1-methylsulfinyl-1-undecene (V) nor 1-methylsulfinyl-2-*t*-butoxyundecane was isolated, although a minor amount of V was present in IV (*vide infra*).



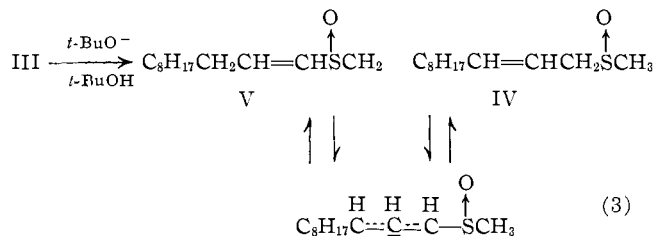
The position of the double bond in IV was assigned on the basis of its n.m.r. spectrum (10% solution in carbon tetrachloride on a Varian A-60 spectrometer) which showed the presence of methylene protons between the double bond and the sulfinyl group (multiplet centered at 6.65  $\tau$ , relative area 1.9), as well as methylsulfinyl protons (sharp band at 7.58  $\tau$ , area 3.0), and allylic protons (multiplet centered at 7.9  $\tau$ , area 2.0). Other features of the spectrum resulted from the vinyl protons (complex multiplet centered at 4.4  $\tau$ , area 1.9) and protons of the alkyl chain (multiplet at 8.7  $\tau$ , area 12.0, and multiplet centered at 9.0–9.1  $\tau$ , area 3.0). The band at 6.65  $\tau$  is at lower field than that observed for protons adjacent to either a sulfinyl group or a double bond. Shifts due to adjacent groups are known to be approximately additive,<sup>10</sup> and this peak is shifted from the absorption region for unactivated methylene protons by an amount about equal to the sum of the shifts produced by the carbon-carbon double bond and the sulfinyl group.

To compare the n.m.r. spectrum of IV with that of an  $\alpha,\beta$ -unsaturated sulfoxide a sample of 1-methylsulfinyl-1-dodecene (VI) (mixture of *cis* and *trans* isomers), b.p. 132° (0.15 mm.) (*Anal.* Calcd. for C<sub>13</sub>H<sub>26</sub>OS: C, 67.7; H, 11.37; S, 13.9. Found: C, 67.6; H, 11.6; S, 13.6) was prepared by the free radical addition of methyl mercaptan to 1-dodecyne and subsequent oxidation of the sulfide. The n.m.r. spectrum of VI differed from that of IV in two important respects. VI did not absorb in the 6.6  $\tau$  region, while its olefinic proton absorption was centered at 3.7  $\tau$  (compared with 4.4  $\tau$  for IV) with none above 3.9  $\tau$ . Thus, by comparison of the peak area at 3.5–3.9 with that at 3.9–4.8  $\tau$ , we estimate that the maximum percentage of V present in the equilibrium mixture of IV and V is 4%. Treatment of 0.043 mole of VI with 0.012 mole of potassium *t*-butoxide in 200 ml. of *t*-butyl alcohol for 5 hr. at room temperature converted it to 1-methylsulfinyl-2-dodecene containing 4% of VI, demonstrating that equilibrium had been attained during the elimination reaction.

That the  $\beta,\gamma$ -isomer is favored under equilibrium conditions was shown independently by deuterium exchange experiments. When 1.0 g. of IV was stirred for 24 hr. at room temperature with 1.0 g. of potassium *t*-butoxide in 10 ml. of *t*-butyl alcohol-*O-d*, exchange occurred at both the  $\alpha$ - and  $\gamma$ -positions to yield C<sub>8</sub>H<sub>17</sub>CD=CHCD<sub>2</sub>SOCD<sub>3</sub> (n.m.r. spectrum indicated relative area of 1.0 at 4.4  $\tau$  and virtual elimination of 6.65 and 7.58  $\tau$  bands). A sample of IV treated with potassium *t*-butoxide in *t*-butyl alcohol under identical conditions was unchanged as shown by its n.m.r. spectrum. These results demonstrate that equilibrium between IV and V is readily established, since deuterium in the  $\gamma$ -position must arise from formation of the  $\alpha,\beta$ -unsaturated isomer followed by conversion to the  $\beta,\gamma$ -unsaturated isomer. It follows that IV is the predominating product in the elimination reaction because it is thermodynamically more stable than V,

(10) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1959, pp. 59–60.

not because it is the kinetically favored product. It seems quite probable that elimination first yields V, which then isomerizes to IV (eq. 3). Russell has re-



ported<sup>11</sup> the similar formation of an  $\alpha,\beta$ -unsaturated compound from 1-methylsulfinyl-2-phenyl-2-hydroxyethane, but in that system a  $\beta,\gamma$ -unsaturated isomer does not exist.

In equilibria between allyl (I, R = H) and propenyl (II, R = H) compounds, determination of the effect of a substituent is complicated by the simultaneous change of two substituents on the double bond, *i.e.*, the double bond of I holds three hydrogens and a -CH<sub>2</sub>X group, whereas that of II holds two hydrogens, a methyl group, and an X group. However, in the equilibrium between IV and V, if we make the reasonable assumption that the effects of the C<sub>8</sub>H<sub>17</sub> and C<sub>9</sub>H<sub>19</sub> groups are essentially identical, then the difference in thermodynamic stability between IV and V is due solely to the difference between the stabilizing effects of the -CH<sub>2</sub>SOCH<sub>3</sub> group and the -SOCH<sub>3</sub> group. Thus, the -SOCH<sub>3</sub> group has a destabilizing effect compared to that of -CH<sub>2</sub>SOCH<sub>3</sub>.

This result strongly suggests that ground-state resonance between the sulfur atom and the adjacent unsaturated system is unimportant, since conjugation would favor the  $\alpha,\beta$ -unsaturated isomer.<sup>1,3</sup> Further discussion will await completion of the studies now in progress.

**Acknowledgment.**—We are indebted to Professor W. von E. Doering for his suggestions and helpful discussions regarding this study. We also thank Dr. T. J. Flautt for assistance with the n.m.r. spectra and Mr. A. L. Voegelé, who performed much of the laboratory work.

(11) G. A. Russell, E. G. Janzen, H. Becker, and F. J. Smentowski, *J. Am. Chem. Soc.*, **84**, 2652 (1962).

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RECEIVED AUGUST 1, 1963

### Popcorn Polymer as a Support in Multistep Syntheses<sup>1</sup> Sir:

The recent publication by Merrifield<sup>2</sup> describing the synthesis of a tetrapeptide on polymer beads prompts us to report at this time experiments carried out independently which demonstrate the feasibility of using a modified "popcorn" polymer as a supporting matrix in repetitive-step syntheses.

In principle it appears that the manipulations involved in the stepwise synthesis of polypeptides and polynucleotides may be materially reduced, thereby rendering possible the construction of more complex substances, if the polymer is held to a solid support throughout the synthetic sequence. To function properly the support should (a) be insoluble in the solvents and inert to the reagents employed, (b) contain a functional group to which the initial monomer unit

(1) This research was supported by the National Science Foundation, grant G25069, and by the Division of General Medical Sciences of the National Institutes of Health, grant GM 10265-01.

(2) R. B. Merrifield, *J. Am. Chem. Soc.*, **85**, 2149 (1963).