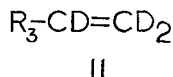
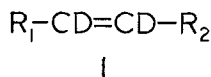


## A NEW METHOD OF SYNTHESIS OF DEUTERATED OLEFINS

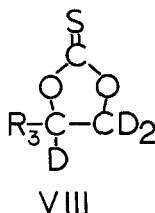
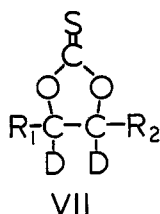
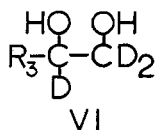
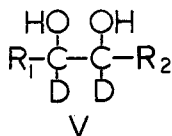
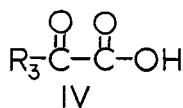
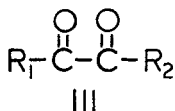
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A New Method of Synthesis of Deuterated Olefins.

There are several procedures available for the preparation of olefins deuterated at the double bond, including stereospecific methods for synthesis of deuterated cis- and trans-olefins<sup>(1)</sup>. We wish to describe a new method for synthesis of both cis- and trans-1,2 disubstituted alkenes (I) and monosubstituted alkenes (II) fully deuterated at the olefinic bond. The latter class of compounds is not readily obtainable by present methods.



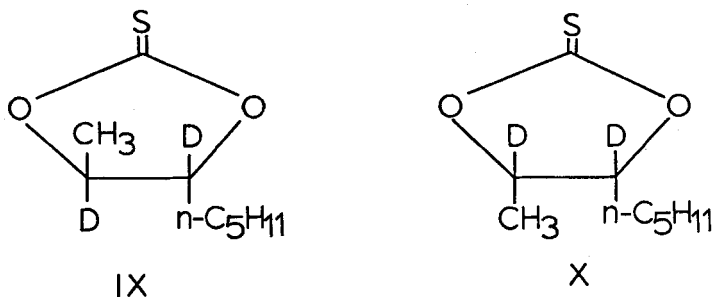
In this method, two easily accessible types of compounds,  $\alpha$ -diketones (III)<sup>(2)</sup> and an  $\alpha$ -ketoacid (IV)<sup>(3)</sup> were reduced with  $LiAlD_4$  to the glycols V and VI respectively. Conversion of the diols to the corresponding thiocarbonates VII and VIII, followed by pyrolysis in trimethyl phosphite according to the method of Corey and Winter<sup>(4)</sup>, afforded the olefins I and II. All reactions were also carried out using non-deuterated compounds.



In the present study, benzil (III,  $\text{R}_1 = \text{R}_2 = \text{C}_6\text{H}_5$ ) was reduced to a mixture of diastereomeric hydrobenzoins (V,  $\text{R}_1 = \text{R}_2 = \text{C}_6\text{H}_5$ ). This was converted to the mixture of cis- and trans-stilbenes via the thiocarbonate VII ( $\text{R}_1 = \text{R}_2 = \text{C}_6\text{H}_5$ ). 2-Ketooctanoic acid (IV,  $\text{R}_3 = \text{n-C}_6\text{H}_{13}$ ) was reduced to 1,2-octanediol- $\text{d}_3$  (VI,  $\text{R}_3 = \text{n-C}_6\text{H}_{13}$ ) which was converted to 1-octene- $\text{d}_3$  (II,  $\text{R}_3 = \text{n-C}_6\text{H}_{13}$ ) via the thiocarbonate VIII ( $\text{R}_3 = \text{n-C}_6\text{H}_{13}$ ).

Corey has shown<sup>(4)</sup> that the thiocarbonate pyrolysis proceeds stereospecifically; i. e., meso- and dl-hydrobenzoin, via their corresponding thiocarbonate, yield cis- and trans-stilbene respectively. Since reduction of benzil gave a mixture of isomeric glycols, the stilbene obtained consisted of a mixture as well. Although the cis- and trans-stilbenes could be separated by vapor phase chromatography, such is not the case with other olefins. In these cases, a separation of either the diastereomeric glycols or thiocarbonates would lead to isomerically pure olefin. In an attempt to achieve this goal, 2,3-

octanedione (III,  $R_1 = \text{CH}_3$ ,  $R_2 = \text{n-C}_5\text{H}_{11}$ ) was reduced to 2,3-octanediol- $\text{d}_2$  (V,  $R_1 = \text{CH}_3$ ,  $R_2 = \text{n-C}_5\text{H}_{11}$ ). The diol was converted to the thiocarbonate VII ( $R_1 = \text{CH}_3$ ,  $R_2 = \text{n-C}_5\text{H}_{11}$ ). Vapor phase chromatography of the latter evinced two peaks of similar size and retention time. Collection of the material afforded two yellowish liquids. That these were the two diastereomeric thiocarbonates IX and X was shown by elemental, infrared, proton magnetic resonance and mass spectrometric analysis.



Therefore, in view of Corey's findings<sup>(4)</sup>,  $\alpha$ -diketones can be a source for deuterated cis and/or trans-olefins. We are currently exploring the scope of this method, especially the preparation of deuterated cyclic and bicyclic olefins.

#### EXPERIMENTAL

##### Starting Materials

2,3-Octanedione was obtained from Eastman, benzil from Matheson, Coleman and Bell, 2-ketooctanoic acid from Columbia Organic Chemicals, thiocarbonyldiimidazole from Pierce Chemical Co. All of the above were used without further purification.

### Spectra

Infrared spectra were measured on a Perkin-Elmer Model 137 spectrophotometer. NMR spectra were determined on a Varian A-60 instrument in  $\text{CDCl}_3$  or  $\text{CCl}_4$ , using TMS as internal standard.

### Glycols (V and VI)

The dicarbonyl compounds were reduced with either  $\text{LiAlH}_4$  or  $\text{LiAlD}_4$  using standard methods<sup>(5)</sup>. The diols were used without purification.

### Thiocarbonates (VII and VIII)

The thiocarbonates were prepared by reacting the glycols with thiocarbonyldiimidazole<sup>(4)</sup>. Products were purified by either column (benzene on silica gel) or vapor phase chromatography (6', 20% SE-30 on 60/80 Chrom W). The thiocarbonate from hydrobenzoin was a white solid; those from the octanediols were pale yellow oils.

The NMR spectrum of VIII ( $\text{R}_3 = \text{n-C}_6\text{H}_{13}$ ) showed two multiplets at 8-9  $\tau$  (13H). The non-deuterated analog gave, in addition, a multiplet at 5-6  $\tau$  (3H) due to protons alpha to the oxygens.

The diastereomers IX and X evinced 2 multiplets at 8-9  $\tau$  (11H) and a singlet at 8.6  $\tau$  (3H). The non-deuterated compounds each showed two multiplets at 8-9  $\tau$  (11H), a doublet at 8.6  $\tau$  (3H), and a multiplet at 5-6  $\tau$  (2H).

The infrared spectra of all thiocarbonates evinced a broad group of bands at 1250-1300 $\text{cm}^{-1}$  (4,6). In addition, the deuterio-compounds showed weak absorption at c. 2200 $\text{cm}^{-1}$ .

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