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Synthesis of Conjugated Diallenes by Double [2,3]-Sigmatropic Rearrangement of Conjugated Diyne Trichloromethanesulfenates

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# SYNTHESIS OF CONJUGATED DIALLENES BY DOUBLE [2,3]-SIGMATROPIC REARRANGEMENT OF CONJUGATED DIYNE TRICHLOROMETHANESULFENATES

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**ABSTRACT**: The preparation of several 2,4-diyne-1,6-diols and their esterification with trichloromethanesulfenyl chloride is described. The thus generated bispropargylic trichloromethanesulfenates undergo spontaneous double [2,3]-sigmatropic rearrangement which leads to the formation of conjugated diallenic trichloromethyl sulfoxides in good to excellent yields.

Allenes are useful intermediates in organic synthesis.<sup>1</sup> The study of allene chemistry is well documented and reviewed.<sup>2</sup> However, in contrast to monoallenes which have received a great amount of interest, the study of diallenes in general and conjugated diallenes in particular have received relatively little attention in the past. This observation is rather surprising in view of the remarkable reactivity demonstrated by such systems.<sup>3</sup> This situation may be the result of the difficulties involved in the preparation of such compounds.

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As early as a quarter century ago, we reported the preparation of a variety of heteroatom bridged diallenic systems which included sulfone bridged diallenes.<sup>4</sup> Furthermore, we have shown that these compounds exhibit some unusual reactivity with regard to either thermal or ionic cyclization.<sup>5</sup>

Synthesis of conjugated diallenes have both mechanistic and synthetic interest. For example, cycloaddition of diallenes with acetylenic compounds yields paracyclophanes.<sup>6</sup> Some of the methods of conjugated diallene synthesis include (i) carbene addition to conjugated dienes followed by cyclopropane ring opening,<sup>7</sup> (ii) metal ion catalyzed coupling of allenyl halides,<sup>8</sup> (iii) base catalyzed prototropic rearrangement of alkynes.<sup>9</sup> In this paper, we wish to present a new approach to the synthesis of conjugated diallenic disulfoxides. These compounds are expected to undergo a variety of cyclization or rearrangement reactions.

The reversible [2,3]-sigmatropic rearrangement of allylic sulfenates to sulfoxides is also known as the Mislow-Braverman-Evans rearrangement.<sup>10</sup> Since its discovery the method has been used extensively in organic synthesis and has played a key role in the synthesis of some natural products such as prostaglandins and leukotriene.<sup>11</sup> Although not as famous as the allylic sulfenate-sulfoxide rearrangement, the propargylic to allenic sulfoxides rearrangement discovered by us some three decades ago<sup>12</sup> has also enjoyed considerable synthetic application.<sup>13</sup> Though the method is successfully used in the synthesis of monoallenes, there is no report on extending the above methodology for the preparation of conjugated diallenes. This may be a result of the poor solubility of diyne diols in the usual aprotic solvents. However, we attempted to overcome this problem by the careful





selection of solvent and reaction conditions which lead to the formation of conjugated diallenyl disulfoxides in a single step in high yields. We also report the procedure as a general route for the synthesis of substituted alkyl and aryl diallenic sulfoxides. For the preparation of required diyne-diols we have employed the procedure reported in the literature.<sup>14</sup>

Starting material diyne diols were prepared by the cuprous chloride-pyridine catalyzed oxidative coupling of propargyl alcohol derivatives by the use of the Glaser reaction in the presence of oxygen (Scheme 1). The various diyne diols prepared, yields and spectral data are presented in Table 1.

The above diyne diols were used for the preparation of the conjugated diallenes. The reaction of diyne diols with trichloromethanesulfenyl chloride in the presence of triethylamine yields the corresponding sulfenate esters which underwent spontaneous double [2,3]-sigmatropic rearrangement affording the desired conjugated diallenes (Scheme 2).

We should note that our attempts to prepare unsubstituted conjugated diallenic disulfoxide by the use of the above procedure was unsuccessful, but this can be interpreted not as a result of the lack of reactivity but rather the result of lack

Entry	Ri	R <sub>2</sub>	Melting Point, °C	Yield (%)	<sup>i</sup> H NMR (δ)	<sup>13</sup> C NMR (δ)
2a°	н	н	117-118	60	4.16 (s 4H)	79.98, 68.38 49.80
2b	Me	Н	93-94	70	4.59 (q, J=6Hz, 2H) 1.47 (d, J=6Hz, 6H)	81.23, 68.10 58.60, 23.86
2c	Me	Me	128-129 <sup>d</sup>	76	1.54 (s, 12H)	83.97, 65.56 66.31, 31.03
2d	Et	Н	114-115	67	4.38 (t, J=6Hz, 2H) 1.75 (m, 4H), 1.02 (t, J=6Hz, 6H)	80.34, 68.82, 63.93, 30.63, 9.33
2e	Et	Me	95-96	78	1.71 (m, 4H), 1.50 (s, 6H), 1.05 (t, J=7Hz, 6H)	82.84, 69.18, 67.45, 36.34 28.94, 8.87
2f°	Ph	Me	132-134	78	7.56, (m, 4H) 7.39-7.28 (m, 6H) 1.67 (s, 6H)	145.98, 128.56 127.78, 125.15 85.28, 68.82 67.56, 33.45

Table 1. Reaction conditions, yields, and spectral data of diyne diols<sup>a,b</sup>

<sup>a</sup> All the compounds showed satisfactory elemental composition based on HRMS. <sup>b</sup> The time of all the reactions was 1 hour except for 2f which was 4 hours. <sup>c</sup> NMR solvent was DMSO-d<sub>6</sub>. <sup>d</sup> reported value, 129-130<sup>14</sup>.



Scheme 2

of stability of the expected product. Finally we should note that the utility of the new conjugated diallenic disulfoxides is now under investigation.

#### **EXPERIMENTAL**

#### **General Procedures**

#### Synthesis of Diyne Diols By Copper (1) Catalyzed Reaction

To a solution of the appropriate propargyl alcohol (0.1 mol) in 10 mL of methanol, 0.5 g of copper (I) chloride and 3 mL of pyridine were added. The contents were stirred under an oxygen atmosphere for the appropriate time (see Table 1). After the reaction was completed, the mixture was cooled in ice and 5 mL conc. HCl were added. To this 25 mL of saturated NaCl were added and the solution was kept overnight in the refrigerator for the completion of crystallisation. The crystals were filtered, washed with ice water and dried in the air. The product was recrystalized from toluene.

#### Synthesis of Conjugated Diallenes

To a suspension of the appropriate diyne-diol (1 mmol) in 10 mL of chloroform, trichloromethanesulfenyl chloride (2 mmol) and triethylamine (2 mmol) were added simultaneously over a period of 5 minutes at 0°C. The reaction mixture was then allowed to warm up to room temperature over a period of 30 minutes and further stirred for one to two hours at the same temperature. At the end of the reaction, 10 mL of diethyl ether were added and the contents transferred to a separatory funnel. The reaction mixture was washed successively with water (3x25 mL), 1%

hydrochloric acid (3x25 mL), saturated NaHCO<sub>3</sub> (3x25 mL) and again with water (2x25 mL). The organic layer was dried over anhydrous MgSO<sub>4</sub> and solvent evaporated in vaccuo.

**4,5-Bis(trichloromethylsulfynyl)-2,3,5,6-octatetraene** (**3b**): Yield 73%. IR (neat): 1960, 1093 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 6.76-5.89 (m, 2H), 2.05-1.73 (m, 6H). <sup>13</sup>C MNR (300 MHz, CDCl<sub>3</sub>) δ: 208.56 δ, 208.41 (=C=), 96.97 (SOCCl<sub>3</sub>). HRMS (MH<sup>+</sup>) C<sub>10</sub>H<sub>9</sub>S<sub>2</sub>O<sub>2</sub>Cl<sub>6</sub>, Found 434.8164, Calc. 434.8175.

**2,7-Dimethyl-4,5-bis(trichloromethylsulfynyl)-2,3,5,6-octatetraene** (**3c**): Yield 88%. IR (neat): 1950, 1110 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 1.98 ( s, 6H), 1.91 (s, 6H). <sup>13</sup>C MNR (300 MHz, CDCl<sub>3</sub>) δ: 207.83 (=C=), 94.31 (SOCCl<sub>3</sub>). HRMS (MH<sup>+</sup>) C<sub>12</sub>H<sub>13</sub>S<sub>2</sub>O<sub>2</sub>Cl<sub>6</sub>, Found 462.8490, Calc. 462.8488.

**5,6-Bis(trichloromethylsulfynyl)-3,4,6,7-decatetraene (3d)**: Yield 75%. IR (neat): 1950, 1105 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 6.65-6.23 (m, 2H), 2.63-2.38 (m, 4H), 1.26-1.19 (m, 6H). <sup>13</sup>C MNR (300 MHz, CDCl<sub>3</sub>) δ: 203.56 (=C=), 93.28 (SOCCl<sub>3</sub>). HRMS (MH<sup>+</sup>) C<sub>10</sub>H<sub>9</sub>S<sub>2</sub>O<sub>2</sub>Cl<sub>6</sub>, Found 462.8381, Calc. 462.8488.

**3,8-Dimethyl-5,6-bis(trichloromethylsulfynyl)-3,4,6,7-decatetraene** (**3e**): Yield 85%. IR (neat): 1960, 1093 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 2.46-2.33 (m, 2H), 2..32-2.29 (m, 2H), 1.98-1.89 (m, 6H), 1.15-1.04 (m, 6H). <sup>13</sup>C MNR (300 MHz, CDCl<sub>3</sub>) δ: 201.35 (=C=), 99.45 (SOCCl<sub>3</sub>). HRMS (M<sup>+</sup>) C<sub>14</sub>H<sub>16</sub>S<sub>2</sub>O<sub>2</sub>Cl<sub>6</sub>, Found 489.8780, Calc. 489.8723.

**2,7-Diphenyl-4,5-bis(trichloromethylsulfynyl)-2,3,5,6-octatetraene** (**3f**): Yield 76%. IR (neat): 1925, 1160 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.41-7.25 (m, 10H), 2.37-2.33 (m, 6H). <sup>13</sup>C MNR (300 MHz, CDCl<sub>3</sub>) δ: 207.83, 206. 80 (=C=), 92.31, 89.56 (SOCCl<sub>3</sub>). HRMS (MH<sup>+</sup>) C<sub>10</sub>H<sub>9</sub>S<sub>2</sub>O<sub>2</sub>Cl<sub>6</sub>, Elemental analysis: Carbon 44.63% (calc. 45.05), Hydrogen 2.81% (calc. 2.73%).

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