

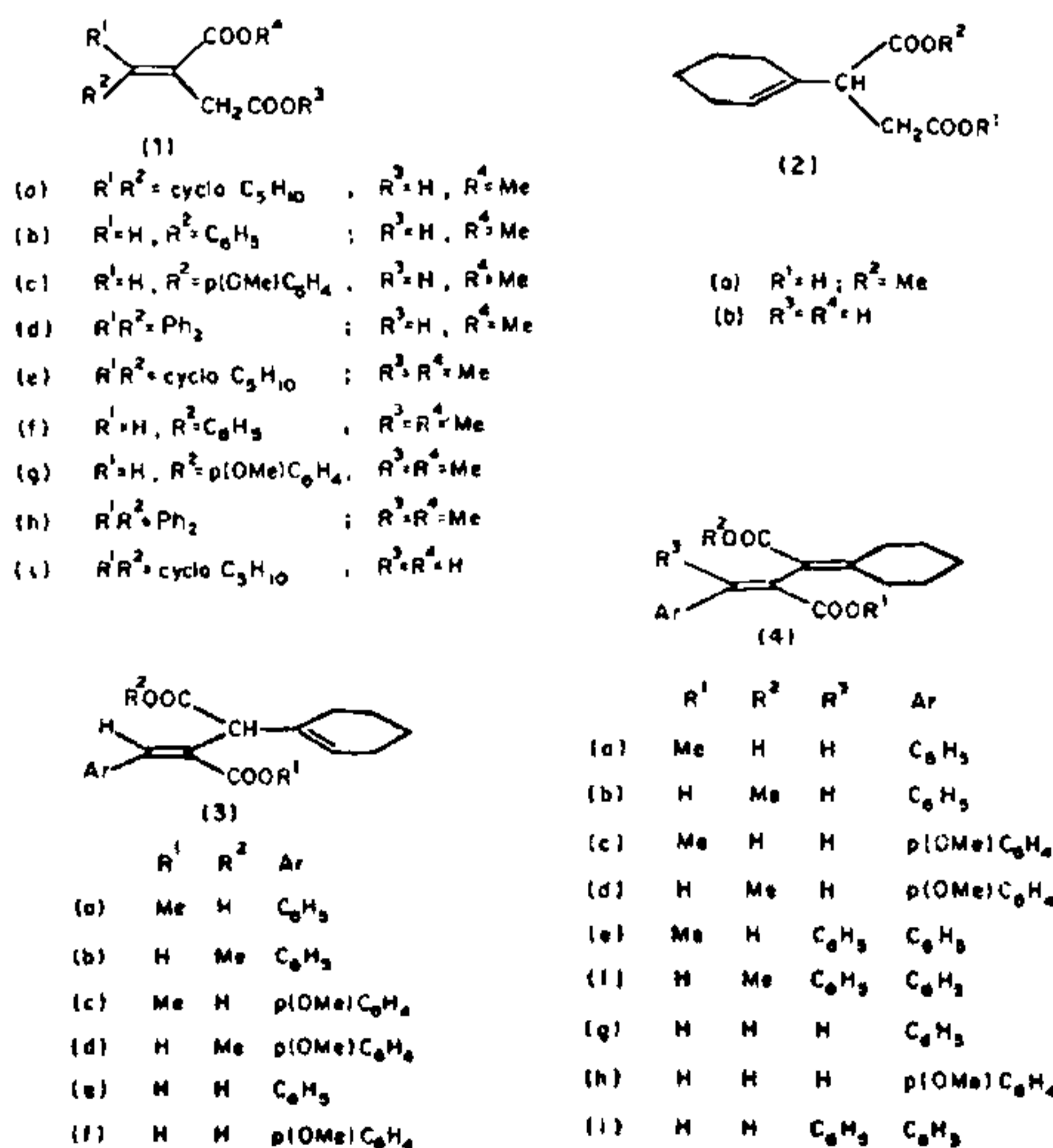
## Migration of double bond in Stobbe reactions

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Stobbe condensation products (acid esters and diacids) of dimethylsuccinate and cyclohexanone show migration of the double bond<sup>1</sup>. We show here that cyclohexylidene-succinate on Stobbe condensation with aromatic aldehydes at 100°C yields the corresponding acid esters and diacids with endocyclic double bond but similar reactions with benzophenone at 100°C always yield the corresponding acid ester and diacid with exocyclic double bond.

MIGRATION of double bond often occurs in Stobbe reactions<sup>1,2</sup>. Stobbe condensation of cycloheptanone with diethylsuccinate (in potassium *t*-butoxide) is reported to yield entirely the acid ester with endocyclic double bond while the dibasic acid obtained on saponification is exclusively exocyclic double-bonded<sup>3</sup>. Stobbe condensation of dimethylsuccinate with cyclohexanone<sup>1</sup> at room temperature (in potassium *t*-butoxide) gives the acid ester **1a** with exocyclic double bond but similar reaction under reflux (in sodium methoxide) gives the acid ester **2a** with endocyclic double bond. [It is reported<sup>1</sup> that the acid ester with exocyclic double bond **1a** on refluxing with potassium *t*-butoxide isomerizes to the acid ester with endocyclic double bond **2a**. Similarly the diacid with exocyclic double bond **1i** on refluxing with potassium *t*-butoxide isomerizes to the diacid with endocyclic double bond **2b**.]



Stobbe condensation (SC) of dimethylcyclohexylidene-succinate<sup>4</sup> and benzaldehyde

Dimethylcyclohexylidene-succinate **1e** (5.0 g) and benzaldehyde (2.4 g) were mixed and added in refluxing potassium *t*-butoxide [generated from potassium (0.9 g) and dry *t*-butanol (23 ml)] under inert and dry conditions and the reaction mixture was refluxed for 1 h. The reaction mixture after usual work-up<sup>4</sup> gave the acid ester **3a** as pale brown viscous oil (5.2 g) which could not be crystallized. [When crystallization of this oily acid ester was tried in benzene-*n*-hexane mixture or benzene-pet. ether mixture, very minute crystals (less than 10% of original amount) were deposited along with a lot of viscous material. The viscous material, on separation by TLC, was found to be 1-cyclohexenyl-2-carbomethoxy-3-phenylprop-2-ene-1-carboxylic acid **3a** on comparison with the authentic sample. On the other hand, the deposited crystals were recrystallized and were found to be 1,1-cyclohexylidene-1-carboxy-2-carbomethoxy-3-phenylbutadiene **4a** from its m.p., m.m.p., and UV, IR and NMR spectra. The equivalent weights of both viscous and crystalline material were within the expected range.]

SC of dimethylcyclohexylidene-succinate and anisaldehyde

Dimethylcyclohexylidene-succinate **1e** (4.0 g) and anisaldehyde (2.4 g) were mixed and added in refluxing potassium *t*-butoxide [generated by dissolving potassium (0.7 g) and dry *t*-butanol (18.0 ml)] under inert and dry conditions for 1 h. The reaction mixture after usual work-up gave the non-crystallizable acid ester **3c** (4.8 g).

SC of dimethylitaconate and cyclohexanone

Dimethylitaconate **1f** (5.0 g) with cyclohexanone (2.1 g) in refluxing potassium *t*-butoxide (22.0 ml) for 1 h gave the acid ester 1-cyclohexenyl-1-carbomethoxy-3-phenylprop-2-ene-2-carboxylic acid **3b** (6.0 g).

SC of *p*-methoxyphenylitaconate and cyclohexanone

*p*-Methoxyphenylitaconate **1g** (5.0 g) with cyclohexanone (1.8 g) in refluxing potassium *t*-butoxide (20 ml) for 1 h gave the acid ester 1-cyclohexenyl-1-carbomethoxy-3-*p*-methoxyphenylprop-2-ene-2-carboxylic acid **3d** (5.9 g).

SC of dimethylbenzhydrylidene-succinate and cyclohexanone

Dimethylbenzhydrylidene-succinate **1h** (5.0 g) with cyclohexanone (1.6 g) in refluxing potassium *t*-butoxide (16.5 ml) for 1 h gave the acid ester methyl-3-carboxy-2,2-cyclohexylidene-4,4-diphenyl-3-butenolate **4b** (5.8 g), crystallized by CCl<sub>4</sub>-hexane, m.p. 151°; (Found: eq. wt., 374.1; C, 76.21; H, 6.08. Required for C<sub>24</sub>H<sub>24</sub>O<sub>4</sub>: eq. wt.,

376.43; C, 76.57; H, 6.43); IR: 1715 (C=O, ester), 1668 (C=O, acid), 1627, 1595 (C=C), 1255 (C=O, *str*); PMR (CDCl<sub>3</sub>):  $\delta$  1.52 (6H, s, alicyclic), 2.27 (2H, s, alicyclic), 2.64 (2H, s, alicyclic), 3.76 (3H, s, -OMe), 7.35 (10H, s, aromatic).

The acid ester on saponification with 8% alc. KOH by refluxing for 8 h gave the diacid **4i** (5.0 g), crystallized by ethanol-water, m.p. 210°; (Found: eq. wt., 180.0; C, 75.89; H, 6.41. Required for C<sub>23</sub>H<sub>22</sub>O<sub>4</sub>: eq. wt., 181.2, C, 76.22; H, 6.12); IR: 1674 (C=O, acid), 1620, 1592 (C=C), 1247 (C-O, *str*); PMR (CDCl<sub>3</sub>):  $\delta$  1.33 (6H, s, alicyclic), 2.09 (2H, s, alicyclic), 2.50 (2H, s, alicyclic), 7.16 (10H, s, aromatic).

#### SC of dimethylcyclohexylidenesuccinate and benzophenone

Dimethylcyclohexylidenesuccinate **1e** (4.0 g) with benzophenone (3.2 g) in refluxing potassium *t*-butoxide (18 ml) for 1 h yielded the acid ester **4e** (5.2 g), and the crude product on saponification with 8% alc. KOH by refluxing for 8 h gave the diacid 3-carboxy-2,2-cyclohexylidene-4,4-diphenyl-3-butenoic acid **4i** (5.0 g), m.p. 210°.

#### Cyclization reactions<sup>5</sup>

The diacid **4i** on cyclization with PPA, conc. H<sub>2</sub>SO<sub>4</sub> at 0°, acetyl chloride, and on internal Friedel-Craft's cyclization with anhydrous AlCl<sub>3</sub> yields the indenone with exocyclic double bond.

The present studies reveal a similar behaviour in dicondensation reactions. Cyclohexylidenesuccinate **1e** on Stobbe condensation with benzaldehyde at 100°C in potassium *t*-butoxide yields the acid ester **3a** in majority with endocyclic double bond, which on saponification gives subsequent diacid **3e** with endocyclic double bond. (The same reaction when carried out at room temperature gives the acid ester **4a** exclusively with exocyclic double bond<sup>6</sup>.) Also, Stobbe condensation of dimethylitaconate **1f** with cyclohexanone at 100°C in potassium *t*-butoxide yields the acid ester **3b** in majority with endocyclic double bond, which on saponification gives subsequent diacid **3e** with endocyclic double bond. (The same reaction when carried out at room temperature<sup>6</sup> yields the acid ester **4b** with exocyclic double bond.) [In the present studies it has also been observed that the Stobbe condensation of cyclohexylidenesuccinate **1e** with anisaldehyde at 100°C in potassium *t*-butoxide yields the acid ester **3c** in majority with endocyclic double bond, which on saponification gives subsequent diacid **3f** with endocyclic double bond. (The same reaction when carried out at room temperature yields the acid ester **4c** with exocyclic double bond<sup>4</sup>.) Also, *p*-methoxyphenylitaconate **1g** on Stobbe condensation with cyclohexanone at 100°C in potassium *t*-butoxide gives the acid ester **3d** in majority with endocyclic double bond, which on saponification

yields subsequent diacid **3f** with endocyclic double bond. (The same reaction when carried out at room temperature<sup>6</sup> yields the acid ester **4d** with exocyclic double bond.)]

Interestingly, the same double bond has been found to be quite stable in Stobbe reactions at 100°C in potassium *t*-butoxide when benzhydrylidenesuccinate **1b** was condensed with cyclohexanone or cyclohexylidenesuccinate **1e** condensed with benzophenone. [The Stobbe condensation of benzhydrylidenesuccinate with acetone and cyclopentanone gave the non-migrated products at room temperature (**4i**, R<sup>1</sup>=R<sup>2</sup>=H and  $\square$  = Me<sub>2</sub> and  $\square$ ). When the same reactions were done in reflux, the same acid esters and diacids were formed (m.p., m.m.p., and UV, IR and NMR spectra), indicating no bond migration in the five-membered cyclopentanone ring or the dimethyl group.] In these cases, the reaction products were exclusively the acid esters (**4e**, **4f**) and the diacid **4i** with exocyclic double bond. (Room-temperature reactions of these molecules always give the acid esters (**4e**, **4f**) and the diacid **4i** with exocyclic double bond<sup>7</sup>.) Thus no migration of double bond has been observed in the acid ester (**4e**, **4f**). This stability of the double bond is attributable to the presence of one more phenyl group in the benzophenone moiety that must be extending its pull over the conjugation in this particular butadienic system.

The diacid **4i** on cyclization with polyphosphoric acid at 100°C, conc. H<sub>2</sub>SO<sub>4</sub> at 0°C, acetyl chloride, or after internal Friedel-Craft's cyclization, did not show the migration of the double bond in the cyclized products<sup>5</sup>.

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## Source and mechanism of carbon dioxide gas occurrences in water wells at and around Vidavaluru, South India

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Carbon dioxide (CO<sub>2</sub>) gas in water wells at Vidavaluru near Nellore in Andhra Pradesh (South India), may have taken the lives of three agriculturists who were negotiating for water in water wells. I propose two