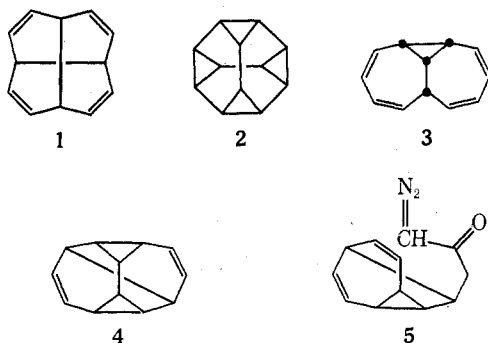


# Communications

## New (CH)<sub>12</sub> Hydrocarbons. Synthesis and Unusual Rearrangements

**Summary:** A synthesis of pentacyclo[5.5.0.0<sup>2,12</sup>.0<sup>6,8</sup>.0<sup>3,9</sup>]dodeca-4,10-diene (4) is described, starting from bicyclo[4.2.1]nona-2,4,7-trien-9-one. Thermolysis of 4 above 160 °C gives benzene, but no products which might be derived from initial retro-Diels-Alder cleavage to tricyclo[5.5.0.0<sup>2,12</sup>]dodeca-3,5,8,10-tetraene (3). Formation of benzene is explained by equilibration of 4 with tetracyclo[5.5.0.0<sup>2,4</sup>.0<sup>3,10</sup>]dodeca-5,8,11-triene (9) by an unusual 6- $\pi$  electron reorganization. Retro-Diels-Alder cleavage of 9 would give bicyclo[6.4.0]dodeca-2,4,6,9,11-pentaene (10), which is known to fragment to benzene. Synthesis of 9 confirms this proposal because 9 rearranges to 4 above 120 °C, thereby demonstrating a low-energy pathway between the two isomers. Novel synthetic steps include (1) a procedure for conversion of  $\alpha,\beta$ -unsaturated esters into  $\alpha,\beta$ -saturated acids in the presence of other olefins via 1-pyrazolin-3-one intermediates; and (2) conversion of tosylhydrazones into alkenes using lithium diisopropylamide at 0–25 °C.

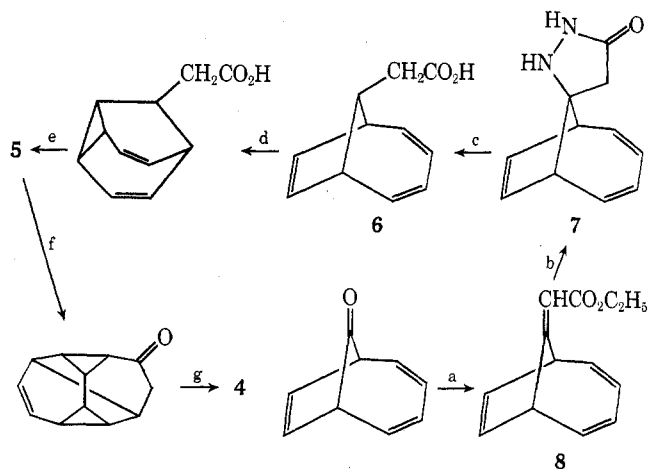
The (CH)<sub>12</sub> isomer 1 is of interest as a potential photochemical precursor of the truncated tetrahedron 2.<sup>1</sup> A possible approach to 1 involves the Cope rearrangement of a divinylcyclopropane 3 which in turn might be available by retro-Diels-Alder cleavage of 4. In this paper we shall describe the synthesis of 4 and its thermal behavior.



Structure 4 can be recognized as a derivative of the barbalane skeleton, accessible by internal ketocarbenoid addition to a double bond in the precursor 5. A convenient synthesis of 4 and 5 is outlined in Scheme I starting from bicyclo[4.2.1]nona-2,4,7-trien-9-one.<sup>2</sup> The key steps in the scheme are the well-precedented di- $\pi$ -methane rearrangement of 6,<sup>2,3</sup> and conversion of 8 into 6. The latter step is accomplished in 82% yield from 7 (57% overall from starting ketone) by oxidative fragmentation via a 1-pyrazolin-3-one intermediate<sup>4</sup> (slow addition of *N*-chlorosuccinimide to 7 dissolved in H<sub>2</sub>O–THF–KOH at –20 °C). Under carefully controlled conditions,<sup>5</sup> this reaction is an efficient general method for reduction of  $\alpha,\beta$ -unsaturated esters.

Vapor phase pyrolysis of 4<sup>6</sup> in a quartz reactor (stirred flow system)<sup>7</sup> does not give detectable amounts of any other (CH)<sub>12</sub> isomer. Instead, the starting material fragments to benzene at temperatures above 160 °C! This highly unusual (although perhaps not unexpected) rearrangement can be explained according to two categories of rationale. In the first category are numerous variations on the theme that some combination of electrocyclic steps will re-

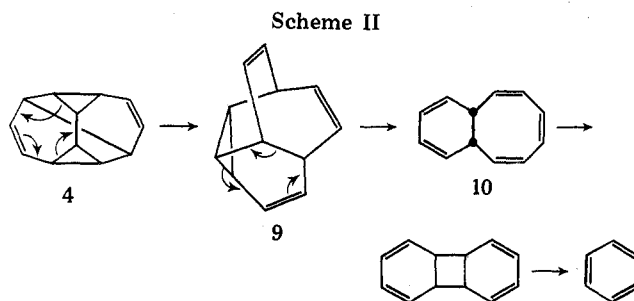
Scheme I<sup>a</sup>



<sup>a</sup> a, (C<sub>2</sub>H<sub>5</sub>O)<sub>2</sub>POCH<sub>2</sub>CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>, NaH; b, H<sub>2</sub>NNH<sub>2</sub>·H<sub>2</sub>O, C<sub>2</sub>H<sub>5</sub>OH,  $\Delta$ ; c, NCS, KOH, THF–H<sub>2</sub>O, –20 °C; d, Ph<sub>2</sub>CO, *h\nu*, C<sub>6</sub>H<sub>6</sub>; e, dicyclohexylamine, (COCl)<sub>2</sub>, CH<sub>2</sub>N<sub>2</sub>; f, CuSO<sub>4</sub>, 80 °C, C<sub>6</sub>H<sub>6</sub>; g, TsNHNH<sub>2</sub>, LiN(*i*-Pr)<sub>2</sub>, 25 °C.

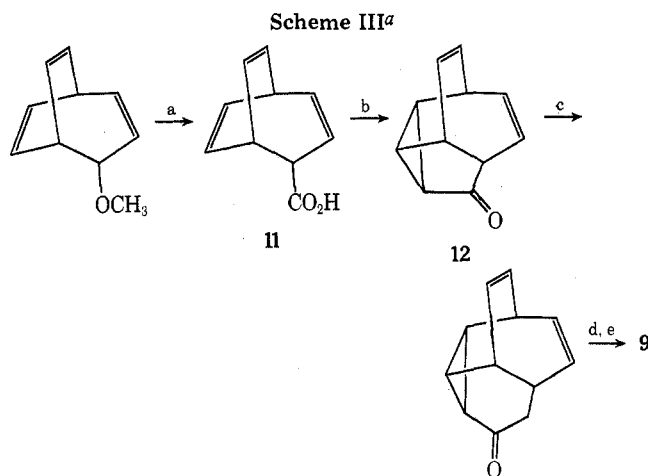
late any (CH)<sub>12</sub> isomer having a continuous chain of all 12 carbons to 12-annulene. As demonstrated by Schröder et al., 12-annulene affords benzene via the valence bond tautomer 10 at 40 °C.<sup>8</sup> In a second category, we shall consider alternatives which do not require formation of a 12-annulene. The most reasonable of these mechanisms involves the novel 6- $\pi$  electron transformation of 4 into 9.<sup>9</sup> Retro-Diels-Alder cleavage of 9 to 10 would then be feasible,<sup>10</sup> and fragmentation to benzene would be the result.

To test the above proposition, we have prepared 9 by the route described in Scheme III. The nontrivial steps in this



sequence are the carboxylation of bicyclo[3.2.2]nonatrienyl anion<sup>11</sup> and ring expansion of a cyclopropyl ketone 12<sup>12</sup> by the excellent method of Taguchi, Yamamoto, and Nozaki.<sup>13</sup> The last step employs a variation of the tosylhydrazone olefin synthesis using lithium diisopropylamide (25 °C, 1–2 h) instead of the usual alkyl lithium reagent.<sup>14,15</sup>

Thermolysis of 9<sup>18</sup> above 160 °C does indeed give benzene, but more significantly, reaction at temperatures between 120 and 150 °C results in complete rearrangement of 9 to 4! Thus, a low-energy thermal pathway connects 4 and 9 and it is reasonable to invoke interconversion of the more stable isomer 4 with 9 at higher temperatures. This experiment provides strong support for the rationale given in Scheme II, and argues against mechanisms involving 12-annulenes. The experiment does not totally rule out the



<sup>a</sup> a, Na/K, THF, CO<sub>2</sub> (58%); b, (COCl)<sub>2</sub>, CH<sub>3</sub>N<sub>2</sub>, copper bronze, benzene, 80 °C (43% overall); c, LiCHBr<sub>2</sub>, BuLi<sup>13</sup> (53% overall); d, TsNHNH<sub>2</sub>, CH<sub>3</sub>OH (62%); e, LiN(*i*-Pr)<sub>2</sub>, THF, room temperature (60%).

possibility that 4 might also equilibrate with 3, but this now appears to be a remote prospect.

**Supplementary Material Available.** Characterization of compounds 6 and 11, together with the experimental details for preparation of these intermediates (4 pages). Ordering information is given on any current masthead page.

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- (5) As reported by Nagata and Kamata, attempted oxidative cleavage of 7 at higher temperatures results in thermal loss of CO and N<sub>2</sub> from the 1-pyrazolin-3-one intermediate to form an olefin.<sup>4</sup>
- (6) Characterization of 4: NMR (CDCl<sub>3</sub>) δ 5.8–5.9 (2 H, m), 2.24 (2 H, br s), 1.1–1.5 (4 H, m), 0.7–1.0 (2 H, m); *m/e* 156. The authors thank Dr. W. Wilber for performing the preparation and identification of 4.
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- (15) We have obtained excellent results using 2–4 mol of LDA for conversion of more typical tosylhydrazones into olefins at 0 °C in THF.<sup>16</sup> In one case, it has been reported that lithium 2,2,6,6-tetramethylpiperidide gives higher yields than LDA.<sup>17</sup> However, we find that LDA is entirely satisfactory for preparation of moderately strained or unstrained olefins.
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- (18) Characterization of 9: NMR (CDCl<sub>3</sub>) δ 6.86 (1 H, dd, *J* = 8.2, 6.4 Hz), 6.24 (1 H, dd, *J* = 8.2, 6.4 Hz), 6.20 (1 H, dd, *J* = 9.0, 5.9 Hz), 6.06 (1 H, dd, *J* = 9.0, 6.8 Hz), 5.42 (1 H, dd, *J* = 9.9, 8.1 Hz), 5.30 (1 H, ddt, *J* = 9.9, 4.9, ca. 0.6 Hz), 3.15 (1 H, m), 2.71 (2 H, m), 1.4–1.8 (3 H, m); exact mass 156.09366 (calcd 156.09390).

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#### Reaction of 1,2- and 1,3-Dicarbonyl Compounds with Dimethyl β-Ketoglutarate. I. Synthesis of Methyl 5,6,7,8-Tetrahydro-5-oxocoumarin-Δ<sup>4(3H),α</sup>-acetate

**Summary:** Reaction of dimethyl β-ketoglutarate (excess) and 1,3-cyclohexanedione in aqueous buffer (pH 6.8) yielded the product of 1:1 stoichiometry, methyl 5,6,7,8-tetrahydro-5-oxocoumarin-Δ<sup>4(3H),α</sup>-acetate.

**Sir:** Reaction of dimethyl β-ketoglutarate 1 with 1,2-dicarbonyl compounds usually proceeds smoothly in aqueous solution (pH 6.8) at room temperature to furnish adducts formed from two molecules of 1 and one molecule of the carbonyl compound. Use of glyoxal (e.g.) yields tetramethyl bicyclo[3.3.0]octane-3,7-dione-2,4,6,8-tetracarboxylate.<sup>1</sup> Other 1,2-dicarbonyl compounds in general give analogous adducts,<sup>1</sup> while in a few cases more complex reaction products have been observed.<sup>2</sup> Cyclic 1,2 diketones yield tetramethyl propellanedione tetracarboxylates.<sup>1,3</sup> The tendency toward 2:1 stoichiometry in this reaction is marked,<sup>1,3</sup> in a few cases, however, 1:1 adducts have been isolated.<sup>4</sup>

It seemed of interest to examine the analogous reaction between 1 and cyclic 1,3 diketones. We now wish to report on a compound obtained from 1 and 1,3-cyclohexanedione 2.

When an aqueous solution of 1 (104.4 g, 0.60 mol) and 2 (22.4 g, 0.20 mol) in citrate/phosphate buffer (pH 6.8) was stirred for several days at room temperature, TLC indicated the presence of a single reaction product in addition to starting materials. Extraction with chloroform and concentration to small volume provided a 45% yield of a pure crystalline compound, mp 123–125°, not changed on recrystallization from chloroform. Elemental analysis and high-resolution mass spectrometry indicated that the new compound had the empirical formula C<sub>12</sub>H<sub>12</sub>O<sub>5</sub>. In contrast to the results with 1,2 diketones, it is evidently produced by reaction of 1 and 2 in a 1:1 ratio with loss of one molecule each of water and methanol.

A plausible scheme leading to two alternative structures for C<sub>12</sub>H<sub>12</sub>O<sub>5</sub> can be easily written (Scheme I). Spectroscopic evidence is compatible with methyl 5,6,7,8-tetrahydro-5-oxocoumarin-Δ<sup>4(3H),α</sup>-acetate 3 and not the α-pyrone 4. The ultraviolet spectrum of 3 [λ<sub>max</sub> 261 nm (log ε 4.06)] is different from those of the authentic α-pyrones 5 and 6 (λ<sub>max</sub> 300<sup>5</sup> and 302<sup>6</sup> nm, respectively) but is similar to that of the ketolactone 7 (λ<sub>max</sub> 271 nm).<sup>5</sup> In the NMR spectrum of 3, two triplets representing the protons of C-6 (2 H) and C-8 (2 H) were observed at δ 2.60 and 2.90, respectively. The multiplet at δ 2.15 was assigned to the two protons of C-7. In addition three singlets were observed which were ascribed to the ester function (δ 3.71), the methylene protons of C-3 (3.81), and the vinyl proton (6.03).

Support for the stereochemical assignment of the exocyclic double bond as that depicted in 3 is obtained by close