

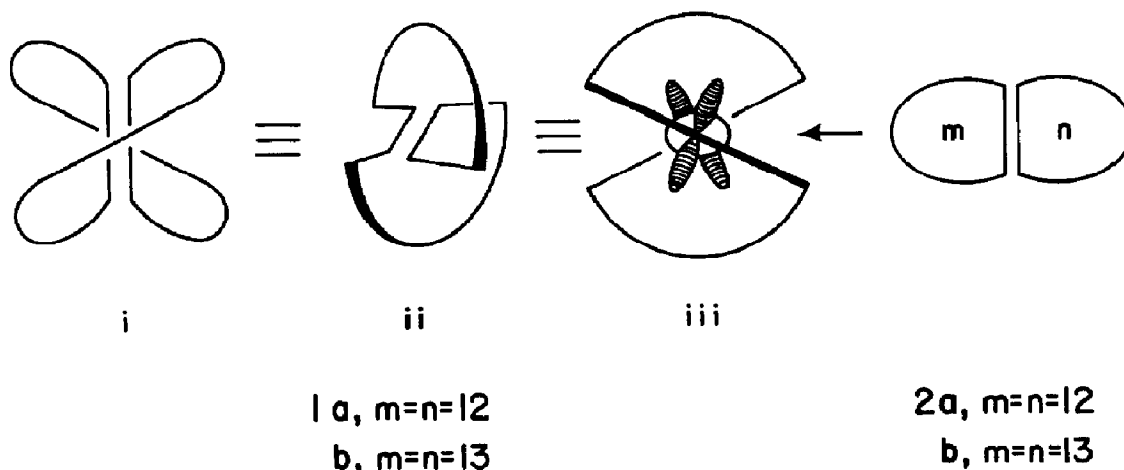
A SHORT ROUTE TO [11.11]BETWEENANENE:  
 CONTRASTING BEHAVIOR IN DIFFERENT RING SIZES<sup>1</sup>

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**Abstract:** Cyclododecanone (**3b**) was converted to [11.11]betweenanene (**1b**) in three steps via 1-cyclododecylcyclododecene (**11b**) and *cis*-bicyclo[11.11.0]tetracens-1(13)-ene (**2b**). The key betweenanene precursor **2b** is also accessible by acid-catalyzed dehydration of the related C<sub>24</sub> spirocyclic alcohol (**7b**).

Our laboratory has been interested in functional groups that are sterically shielded by molecular chains. One such class is represented by *trans*-bicyclic olefins like **1**, in which both faces of the double bond are spanned by aliphatic chains that arch over, or "dome," the π bond. The simplified perspective **ii** shows a planar olefinic unit, but shorter chains could twist the π-system (e.g. **iii**) and also could alter hybridization at each unsaturated carbon. Our plans to synthesize "double domed" olefins were anticipated independently by Marshall *et al.*<sup>2</sup> and by Nagasaki *et al.*,<sup>3</sup> who reported the first prototypes. Marshall's group coined the term "betweenanene" and prepared the first example **1a** (m,n represent the number of atoms in each ring) by stepwise elaboration of a monocyclic precursor.<sup>2</sup> The Nagasaki approach was to synthesize the *cis* (i.e. non-domed) analogs **2**, which they then isomerized to the domed isomer by irradiation.<sup>3</sup> This photic conversion broadens access to domed olefins because the *cis* isomer might be the simpler synthetic target.<sup>4a</sup>



A recent communication by Marshall *et al*<sup>4b</sup> on isomerizations in large-ring, bicyclic alkenes prompts us to report our (contrasting) findings with an analogous, but larger, ring system. Aiming towards the synthesis of [10.10]betweenanene (i.e. 1a) or its cis counterpart (2a), Marshall reported that acid treatment of 4a or acetolysis of the spirocyclic mesylate 7a produced in each case a mixture of 11a and 12a but no 1a or 2a.<sup>5</sup> Total absence of the latter two olefins led them to conclude that ring expansion of cations 8 and 9 to cation 10 is unfavorable. Also, they separately synthesized olefin 13a and report it to be unchanged by their acid treatment. Their findings suggest that cationic isomerizations, though attractive for their brevity, are not viable routes to double domed olefins or to their cis counterparts.

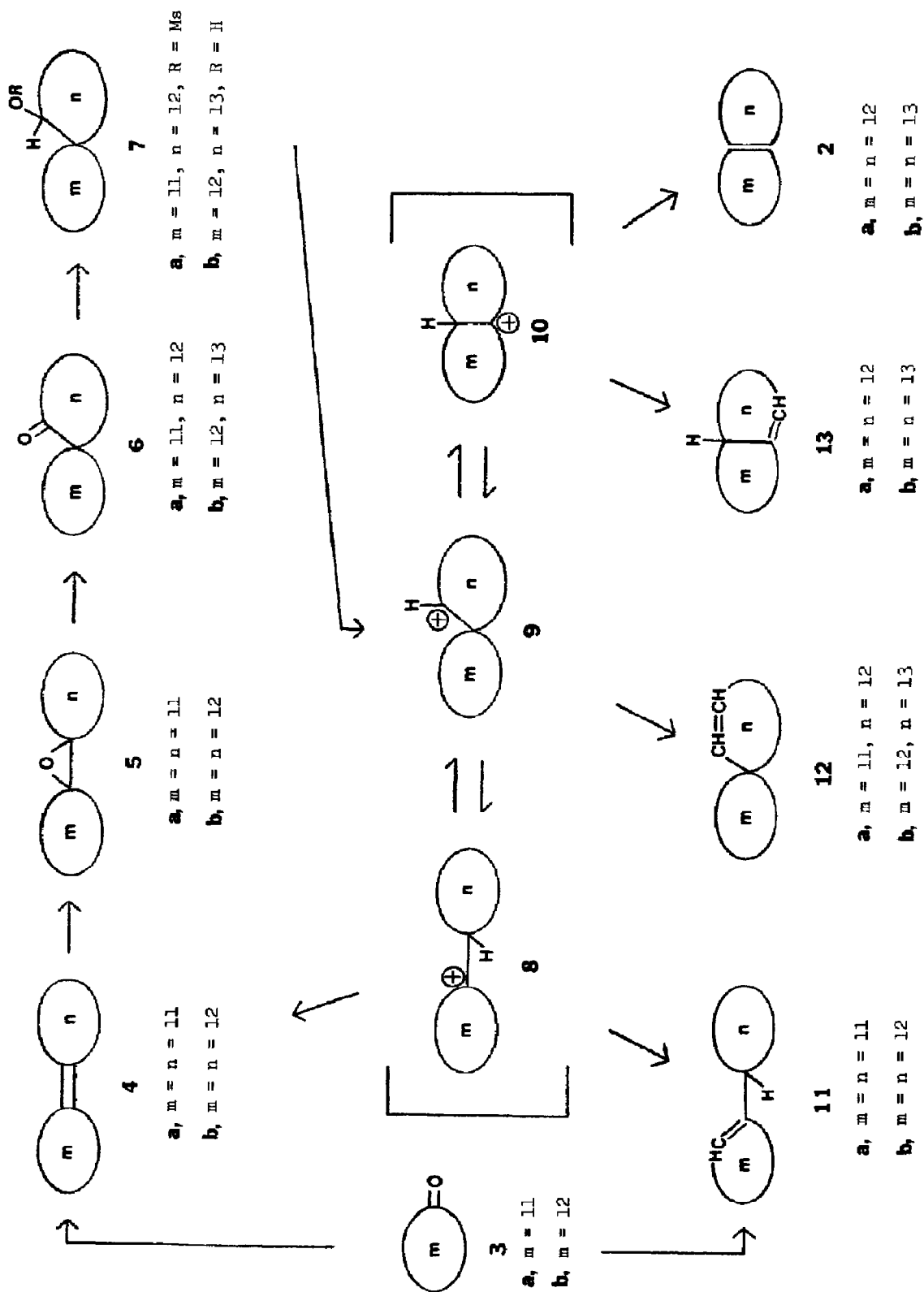
In our pursuit of olefins 1b and 2b, we dehydrated spiroalcohol 7b, which contains one more CH<sub>2</sub> in each ring than does Marshall's substrate. In contrast to Marshall's results, our product mixture included olefins derived from cation 10.

To obtain spiroalcohol 7b, we prepared and epoxidized (63%) the known<sup>6</sup> olefin 4b with *m*-chloroperoxybenzoic acid. The oxide, 5b, was rearranged with BF<sub>3</sub> to spiroketone 6b (80%) and then reduced to alcohol 7b with LiAlH<sub>4</sub> (77%). Dehydration of 7b in CH<sub>2</sub>Cl<sub>2</sub> with HClO<sub>4</sub><sup>7</sup> gave, after 4.25 hr and in quantitative yield, a mixture of eight olefins, viz.: 4b (1%); 11b (E+Z; 49%); 12b (E; 26%); 13b (E+Z; 19%); 2b and 12b (Z) (5% combined).<sup>8,9,10</sup> Olefins 2b and 13b reveal that in our ring size the spirocation 9 rearranges to tertiary cation 10 as well as to 8.

We found that the olefin proportions changed when the dehydration reaction was allowed to stand longer. For e.g., when monitored for 47 hr, the amounts of 13b increased, 4b and 11b decreased, and 12b increased at first but then decreased. These trends suggested that cation 8 does, indeed, rearrange to cation 10.

To test this view and to exploit it in a simple synthesis of betweenanene 1b, we coupled cyclododecanone reductively (TiCl<sub>4</sub>/Zn) to a 90:10 mixture of 11b (E+Z) and 4b.<sup>11</sup> These olefins and neat trifluoroacetic acid formed a heterogeneous mixture, which was shaken overnight at room temperature. The complex product mixture, virtually all olefins, contained 2b and 13b (E+Z). We isolated the desired olefin 2b in 20% yield after column chromatography and recrystallization.<sup>12</sup> Direct irradiation<sup>3</sup> of 2b in heptane gave us [11.11]betweenanene (1b).<sup>13</sup> This double domed olefin was easily separated (50% yield) from the other products of photolysis by column chromatography on AgNO<sub>3</sub>-impregnated silica gel, thus completing its three-step synthesis from cyclododecanone (viz. 3b → 11b → 2b → 1b).

The marked difference in behavior between our C<sub>24</sub> substrates and the C<sub>22</sub> alkenes reported by Marshall *et al* indicates that predictions for other homologs should not be made at this time. Each ring size may require individual examination.



## References and Notes

- Supported by the National Institutes of Health and the National Science Foundation.
- Marshall, J. A. and Lewellyn, M. E., *J. Am. Chem. Soc.*, 1977, 99, 3508-3510.
- (a) Nakazaki, M., Yamamoto, K., and Yanagi, J., *J. Chem. Soc., Chem. Commun.*, 1977, 346-347; (b) Nakazaki, M., Yamamoto, K., and Yanagi, J., *J. Am. Chem. Soc.*, 1979, 101, 147-151.
- (a) Marshall, J. A., Bierenbaum, R. E., and Chung, K-H., *Tetrahedron Lett.*, 1979, 2081-2084; (b) Marshall, J. A., Black, T. H., and Shone, R. L., *Tetrahedron Lett.*, 1979, 4737-4740.
- No information about E-Z isomerism was provided.
- McMurry, J. E., Fleming, M. P., Kees, K. L., and Krepski, L. R., *J. Org. Chem.*, 1978, 43, 3255-3266.
- Dehydrations under a variety of other conditions also gave olefins from cation 10.
- The olefin mixture was analyzed by GLC,<sup>9</sup> and by TLC on AgNO<sub>3</sub>-impregnated silica gel. Separations by column chromatography (AgNO<sub>3</sub>-silica gel) and by preparative TLC ultimately gave the following olefins analytically pure:<sup>10</sup> 2b; 4b; 11b (E+Z); 12b (E); 13b (E or Z). The carbon skeletons and the double bond location were established by <sup>13</sup>C NMR and by catalytic hydrogenations to the corresponding expected saturated hydrocarbons. On this basis, and on some additional chemical evidence, we believe the seventh and eighth olefins (formed here in trace amount and not isolated) are 12b (Z) and the other geometric isomer of 13b.
- GLC was performed on a liquid-crystal liquid phase N,N'-bis(p-butylxybenzylidene)- $\alpha,\alpha'$ -bi-p-toluidine (BBBT). See Janini, G. M., Muschik, G. M., and Zielinski, Jr., W. L., *Anal. Chem.*, 1976, 48, 809-813. Silicone liquid phases such as SE-30 failed to reveal all the components and resulted in deceptively simple chromatograms.
- Characterization included C and H analyses, IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR.
- Modeled on a procedure developed for acyclic ketones by Mukaiyama, T., Sato, T., and Hanna, J., *Chem. Letters*, 1973, 1041-1044.
- Interestingly, although the tetrasubstituted olefin 2b was produced in synthetically useful amounts in this heterogeneous reaction, it is a minor component in homogeneous acidic medium. For example, we separately isomerized olefin 2b to as much as 94% of 13b (E+Z) with BF<sub>3</sub>·Et<sub>2</sub>O in refluxing benzene solution. We think the insolubility of our C<sub>24</sub> olefins in CF<sub>3</sub>CO<sub>2</sub>H, and the high crystallinity of 2b in particular, strongly influence the olefin ratios.
- Physical constants for these target olefins are:<sup>10</sup>  
1b: mp 103-104°C; IR (CHCl<sub>3</sub>)  $\nu$  2920, 2840, 1460 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  1.05-1.70 (m, 36H), 1.70-2.08 (m, 4H), 2.30-2.70 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  24.85, 25.12, 25.16, 27.15, 27.73, 30.82, 134.87; UV (heptane),  $\lambda_{\max}$  212 ( $\epsilon$  = 6700), 208 ( $\epsilon$  = 6700), 202 (sh,  $\epsilon$  = 5800) nm. Inert to hydrogenation with Pt in HOAc-heptane, 3 atmos., room temperature.  
2b: mp 129-130°C; IR (CHCl<sub>3</sub>)  $\nu$  2920, 2840, 1460 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  1.15-1.65 (m, 36H), 1.80-2.14 (m, 8H); <sup>13</sup>C NMR (CDCl<sub>3</sub>),  $\delta$  23.98, 24.98, 25.61, 26.66, 26.97, 30.56, 133.90; UV (heptane),  $\lambda_{\max}$  200 ( $\epsilon$  = 10,100) nm.

(Received in USA 27 May 1980)