

## CARBOCATION ROUTES TO LARGE BICYCLIC OLEFINS

### A THREE-STEP SYNTHESIS OF [11.11] BETWEENANENE

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(Received in U.S.A. 8 October 1982)

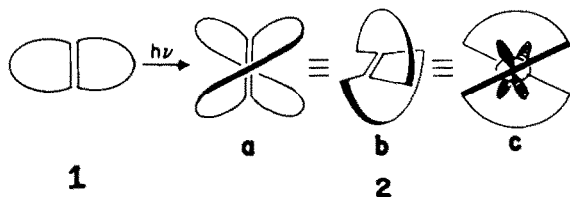
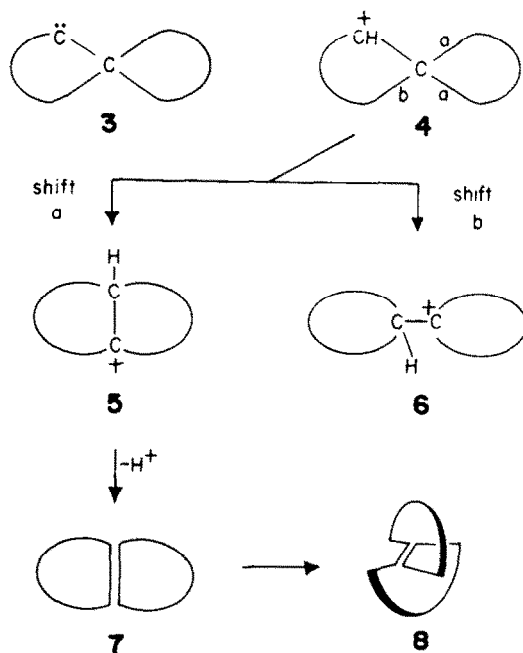
**Abstract**—Our objective was to explore access to bicyclic tetrasubstituted olefins by rearrangement of large spirocyclic cations. Such olefins serve as precursors for subsequent photic conversion to domed bicyclic alkenes (betweenanenes). We synthesized the spirocyclic alcohol 13-hydroxyspiro[12.11]tetracosane (**14a**) and dehydrated it under various acidic and non-acidic conditions to olefin mixtures containing these components: cyclo-dodecylidene-cyclododecane (**11**), (*E*)- and (*Z*)-1-cyclododecylododecene (**12**), (*E*)- and (*Z*)-spiro[12.11]tetracos-13-ene (**16**), (*Z*)-bicyclo[11.11.0]tetracos-1(13)-ene (**19**), (*E*)- and (*Z*)-bicyclo[11.11.0]tetracos-1-ene (**20**). The olefin proportions varied according to the dehydration media and, in acid solution, varied with time. Rearrangement of the spirocyclic precursor to the non-fused, bicyclic skeleton (present in olefins **11** and **12**) is favored kinetically; but, on prolonged treatment in acid, the fused bicyclic skeleton (present in alkenes **19** and **20**) increases in amount at the expense of **11** and **12**. We also examined acid-catalyzed isomerizations of olefin **19** as well as of **11** and **12** mixtures that ranged from pure **11** to those rich in **12**.

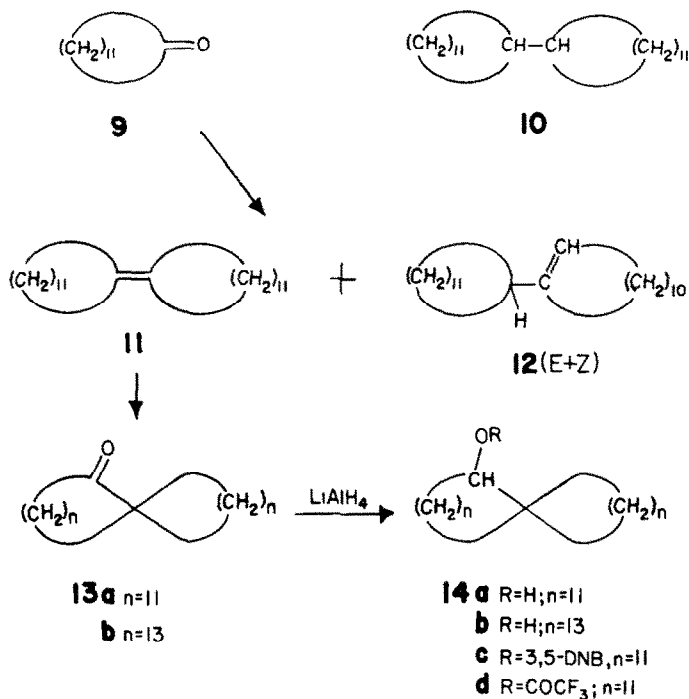
In the fused bicyclic series, equilibration in benzene solution containing  $\text{BF}_3$ -etherate favors trisubstituted alkene **20** (*E* + *Z*) over its tetrasubstituted isomer **19** by a ratio of ca 93:7. To overcome this unusual stability order in our quest for **19**, we examined olefin isomerizations in heterogeneous acidic media. We developed conditions that produced mixtures containing ca 50% of the desired alkene **19**. In these heterogeneous isomerizations, crystallinity and relative solubility appear to be among the important factors that govern product composition. We converted **19** to the unknown [11, 11]betweenanene (**28**) by photic isomerization in heptane. Our ultimate, three-step synthesis of this domed olefin (viz cyclododecanone  $\rightarrow$  [**11** + **12**]  $\rightarrow$  **19**  $\rightarrow$  **28**) makes it readily accessible and suggests that heterogeneous media might find use in other instances where a desired isomer is not favored in homogeneous equilibrations.

Research groups in the U.S.,<sup>1</sup> in Japan,<sup>2</sup> and in Italy<sup>3</sup> have reported syntheses of *trans*-bicyclic olefins like **2** (called "betweenanenes"), in which both faces of a double bond are shielded by chains of atoms that arch over, or "dome," the  $\pi$  bond. Some of these syntheses involved elaboration of a second ring onto a suitably structured monocyclic precursor, whereas other approaches involved preparation of the related *cis*-bicyclic analog (**1**) followed by its photic isomerization to the doubly *trans* (i.e. domed) isomer.

For analogs of **1** that contain no photolabile functionalities, this last route to domed molecules holds appeal because strategy can be aimed toward the *cis*-isomer **1**, which is usually the simpler synthetic target. One objective in our laboratory was to explore possible access to type **1** (and, therefore, ultimately to type **2**) via skeletal isomerizations of spirocyclic carbenes like **3** and of spirocyclic cations like **4**. Recently, we described carbenic systems of type **3**, whose generation and behavior are of interest to carbene chemistry.<sup>4</sup> We now report on cationic rearrangements in a spirocyclic, neopentyl-type cation **4**. Specifically, we found that such isomerizations can convert **4** to cations like **5** and **6**,

which produce alkene **7** as well as other olefins. Exploiting this aspect, we developed a very short route (three steps) to a symmetrical betweenanene structure (type **8**) with thirteen carbons in each ring. Some of our preliminary results were reported.<sup>5</sup> We now disclose full details as well as extension of our cationic isomerization studies.





Scheme 1.

**Syntheses.** As a precursor to a cation like **4**, we chose spiroalcohol **14a**, prepared as shown in Scheme 1. Reductive coupling of cyclododecanone (**9**) preferentially gave the known dumbbell-shaped olefin cyclododecylidene-cyclododecane (**11**) under a variety of conditions described earlier (e.g.  $\text{TiCl}_4/\text{Py}/\text{dioxane}/\text{Zn}$ ).<sup>4</sup> Importantly, we found conditions for this coupling ( $\text{TiCl}_4/\text{dioxane}/\text{activated Zn}$ )<sup>6</sup> that provides mixtures of olefins **11** and **12** highly favoring (e.g. ca 90%) the trisubstituted isomer **12**, which can be separated from **11** by preparative TLC. From these coupling reactions, **12** is obtained as a mixture of *E*- and *Z*-isomers, resolved on GLC. The geometric isomer with shorter retention time (designated *EZ*-1) was present in minor proportion relative to the geometric isomer with longer retention time (designated *EZ*-11) (e.g. typical ratio 5:85, respectively). However, we could not unequivocally tell which was *E* and which was *Z*.<sup>7</sup> The skeletal structure of **12** was confirmed by catalytic hydrogenation of the *E* + *Z* mixture to a single, new alkane (1,1'-bicyclododecane **10**) identical (TLC, GLC, mixture m.p.) to the alkane we obtained by hydrogenation of the known olefin **11**. That **12** has a trisubstituted olefin link was established by <sup>1</sup>H and <sup>13</sup>C NMR (see experimental). For example, the proton-decoupled <sup>13</sup>C spectrum showed two olefinic carbons ( $\delta$ 124.48 and 143.16).<sup>8</sup> Single frequency, off-resonance decoupling revealed that one olefinic carbon was quaternary and the other carried one hydrogen. Finally, a signal at  $\delta$ 37.97 (allylic region) arose from a C bearing one H.

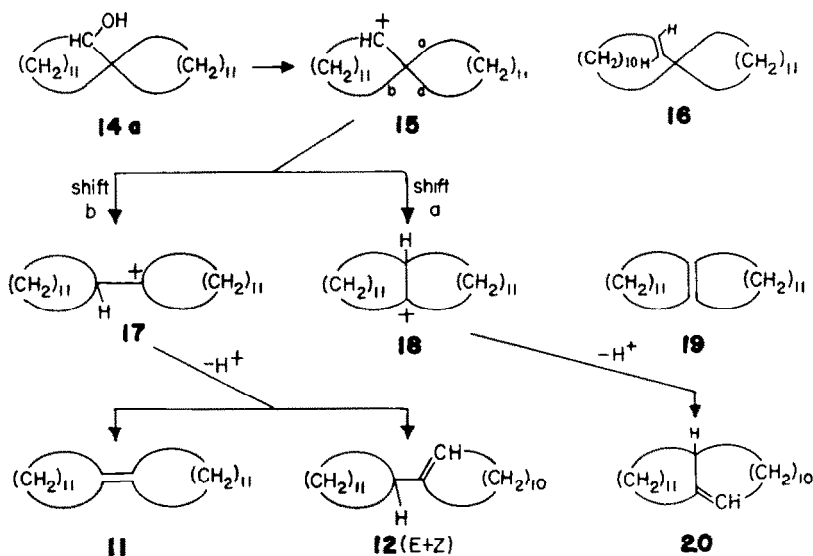
The ability to favor either **11** or **12** in the reductive coupling of ketone **9** has obvious synthetic utility and played an important role in our present work, as will become evident later. We hypothesize that zinc chloride, formed from  $\text{TiCl}_4$  and zinc in the mixture, catalyzed isomerization of **11** to **12**. With pyridine present to scavenge the  $\text{ZnCl}_2$  as it is formed (Lenoir's technique<sup>9</sup>),

olefin **12** does not form. This view is supported by isomerization experiments to be discussed later.

We transformed alkene **11** to known spiroketone **13a** as reported<sup>4</sup> and reduced this ketone to spiroalcohol **14a** (77% yield) with lithium aluminum hydride. The 3,5-dinitrobenzoate (**14c**) and trifluoroacetate (**14d**) esters were also prepared to serve as possible precursors for cation generation. The proton decoupled <sup>13</sup>C NMR spectrum of alcohol **14a** showed 21 signals, one of which was typical of a secondary carbinyl C ( $\delta$ 77.37).<sup>8</sup> The <sup>13</sup>C spectrum also revealed a single quaternary C with  $\delta$ 42.00, a value reasonable for a tetrasubstituted C alpha to a carbinyl C.<sup>8</sup> These data support the view that our alcohol has the expected unrearranged structure **14a**. Similar reduction of the homologous, known<sup>4</sup> spiroketone **13b** gave us the corresponding spiroalcohol **14b** in 81% yield.

When a suspension of solid alcohol **14a** in neat trifluoroacetic acid was stirred at room temperature, the alcohol dissolved and, after a few minutes, a white solid precipitated. Workup of the mixture after 12 min gave a crude product that showed five spots on silver nitrate-impregnated silica gel TLC ( $\text{AgNO}_3\text{-SiO}_2$ ) and six peaks on GLC. Listed in order of elution, the six peaks had relative areas 4%, 53%, 31%, 6%, 4% and 2%. The first two components (isolated as a pair by TLC) were identified as the geometric isomers of alkene **12** (*EZ*-1 and *EZ*-11). Presumably, they arise by Wagner-Meerwein rearrangement of bond **b** in the secondary cation **14** and then proton expulsion from the tertiary cation **17** (Scheme 2).

The third component (31%) was also isolated by TLC and was identified as trisubstituted alkene **20** (*EZ*-11)<sup>7</sup> from the following spectral data. The <sup>1</sup>H NMR showed a 1:5:38 intensity ratio for vinylic, allylic, and simple aliphatic signals, in agreement with structure **20**. And, the vinylic proton ( $\delta$ 5.20) was a triplet ( $J = 7$  Hz) in accord with its



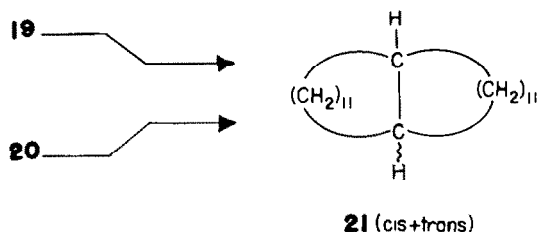
location next to an allylic methylene. In the  $^{13}\text{C}$  NMR, the broad band proton-decoupled spectrum showed two olefinic C's ( $\delta$ 125.90 and 142.92). The lower field alkene C is quaternary and the higher field C bears one H, according to a single frequency, off-resonance decoupling experiment. The same decoupling experiment revealed one tertiary allylic C ( $\delta$ 45.71). Alkene **20** fits all the data and logically arises from cation **18**, itself an outcome of an alternative Wagner-Meerwein shift (bond a) in original cation **15**. We believe our compound **20** (*EZ*-11) is a single geometric isomer (only one component via TLC and GLC), but we could not assign to it the *E* or *Z* configuration.<sup>10</sup>

The fourth and fifth components (6% and 4%, respectively) were identified as known (*E*)-spiroalkene **16** and tetrasubstituted olefin **11** by chromatographic comparison ( $R_f$  on TLC and peak enhancement on GLC) with authentic samples.<sup>4</sup> These two components logically arise from cations **15** and **17**, respectively.

The sixth component was present in too small a proportion (2%) to permit isolation and identification. However, this product was produced in larger amounts in the reaction we discuss next, so we were able to assign its structure as tetrasubstituted, *cis*-alkene **19**.

In other trifluoroacetic acid-catalyzed dehydrations of spiroalcohol **14a**, we did not work up the mixture immediately after all the substrate had been consumed, but instead we continued the stirring. Workup after 16.5 hr gave the same six products but in new proportions; an unidentified seventh component was also formed. Listed in order of elution on GLC, the constituents were: alkene **12** (*EZ*-1, 2%), alkene **12** (*EZ*-11, 29%), alkene **20** (*E* or *Z*, 34%), (*E*)-spiroalkene **16** (7%), dumbbell alkene **11** (12%), tetraalkylated *cis*-olefin **19** (14%), and an unidentified component (2%). We isolated and identified the target *cis*-olefin **19** as follows.

Crystallization of the crude product gave a white solid consisting of **11** and **19** in a 2:1 ratio. Isomer **19** was obtained pure by preparative TLC of this mixture. A broad-band proton decoupled  $^{13}\text{C}$  NMR of **19** showed only seven signals and so indicated a structure of high symmetry. One signal ( $\delta$ 133.90) was typically olefinic and



was quaternary according to a single-frequency off-resonance decoupling experiment. The  $^1\text{H}$  NMR of **19** showed no vinylic protons; and, as expected for structure **19**, the allylic and aliphatic protons had the intensity ratio of 1:4.5. That alkenes **19** and **20** have a common carbon skeleton was demonstrated by catalytic hydrogenation. Each was separately reduced to a mixture of the same two saturated hydrocarbons, which logically are *cis*- and *trans*-bicyclo[11.11.0]tetracosane (**21**). Not surprisingly, these two alkanes were produced in slightly different proportions from each alkene precursor.

The formation of olefins **11** and **12** (with a non-fused bicyclic skeleton) and of olefins **19** and **20** (with a fused bicyclic skeleton) among the dehydration products from spiroalcohol **14a** indicates that cation **15** does rearrange to both tertiary cations **17** and **18** (Scheme 2).<sup>11</sup> Furthermore, the change in product composition with time showed that these alkenes can interconvert under the reaction conditions.

To learn whether the product ratios could be controlled to favor a specific skeleton or a specific olefin, we examined the response of spiroalcohol **14a** to various dehydration reagents and also the isomerization of individual olefins and of olefin mixtures. These studies proved informative and ultimately allowed us to develop a practicable route to our target betweenanene. Our results are shown in Table 1.<sup>12</sup>

**Dehydrations of spiroalcohol 14a.** Entries 1 and 2 in Table 1 refer to trifluoroacetic acid medium and summarize the data discussed earlier. Entries 3-8 reveal the outcome for dehydrations brought about by boron trifluoride etherate in methylene chloride, by refluxing

Table 1. Product ratios from dehydrations of spiroalcohol **14a** and from acid isomerizations of olefins<sup>a</sup>

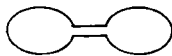
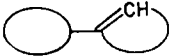


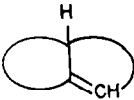
									
		<b>11</b>	<b>12</b>	<b>16</b>	<b>19</b>	<b>20</b>			
Entry	Substrate	Medium	Time (h)	Products					
				$\frac{12}{(EZ-1)^b}$	$\frac{12}{(EZ-1)^c} + \frac{20}{(EZ-1)^e}$	$\frac{20}{(EZ-1)^d}$	(E)-16	11	$\frac{19}{(Z)-16}$
1	alcohol <u>14a</u>	CF <sub>3</sub> CO <sub>2</sub> H	0.2	4	53 <sup>f</sup>	31	6	4	2 <sup>g</sup>
2 <sup>h</sup>	"	"	16.5	2	29 <sup>f</sup>	34	7	12	14 <sup>g</sup>
3	"	BF <sub>3</sub> ·Et <sub>2</sub> O CH <sub>2</sub> Cl <sub>2</sub>	20	2	40 <sup>f</sup>	38	14	1	5 <sup>g</sup>
4 <sup>i</sup>	"	(Me) <sub>2</sub> SO	13	4	45 <sup>f</sup>	10	35	5	1 <sup>g</sup>
5	"	POCl <sub>3</sub> pyridine	7.5	4	41 <sup>f</sup>	5	39	11	--
6	"	HClO <sub>4</sub> hexane	96	3	72	10	11	3	1 <sup>g</sup>
7	"	HClO <sub>4</sub> CH <sub>2</sub> Cl <sub>2</sub>	4.25	3	52 <sup>j</sup>	16	22	3	3 <sup>k</sup>
8	"	"	8.5	2	38 <sup>j</sup>	21	28	3	8 <sup>k</sup>
9 <sup>h</sup>	"	"	21.5	1	26 <sup>j</sup>	31	26	1	14 <sup>k</sup>
10	"	"	47	1	18 <sup>j</sup>	45	17	<1	18 <sup>k</sup>
11	olefin <u>11</u>	"	4	3	62 <sup>l</sup>	10	20	3	2
12	"	"	20	1	28	27	30	1	13
13 <sup>m</sup>	"	"	48.5	trace	19 <sup>n</sup>	38	25	trace	17 <sup>k</sup>
14 <sup>m</sup>	"	"	72.5	trace	16 <sup>n</sup>	45	20	trace	19 <sup>k</sup>
15 <sup>m</sup>	"	"	96	trace	16 <sup>n</sup>	52	14	trace	18 <sup>k</sup>
16	olefin mixture <u>12(97%):11(3%)</u>	CF <sub>3</sub> CO <sub>2</sub> H	5.75	3	40	4	--	37	16 <sup>o</sup>
17	"	"	12.5	2	37	8	<1	34	19 <sup>o</sup>
18 <sup>h</sup>	"	"	17.5	2	36	6	<1	35	21 <sup>o</sup>
19 <sup>n</sup>	"	"	23	2	53	15	<1	20	22 <sup>o</sup>
20	olefin <u>19</u>	BF <sub>3</sub> ·Et <sub>2</sub> O benzene	1.75	--	14 <sup>p</sup>	79	--	--	7
21	olefin <u>11</u>	"	3	5	88	--	--	7 <sup>q</sup>	--
22 <sup>r</sup>	olefin mixture <u>12(93%):11(7%)</u>	CF <sub>3</sub> CO <sub>2</sub> H 6% heptane	27.5	--	2 <sup>s</sup>	69	--	1	24 <sup>t</sup>
23	"	CF <sub>3</sub> CO <sub>2</sub> H 4% heptane	21	1	2 <sup>s</sup>	21	--	24	52
24 <sup>r</sup>	"	CF <sub>3</sub> CO <sub>2</sub> H 6% heptane	24	2.0	2 <sup>s</sup>	42	<1	4	47 <sup>t</sup>

Table 1. (Contd).

Entry	Substrate	Medium	Time (h)	Products					
				12 (EZ-1) <sup>b</sup>	12 (EZ-11) <sup>c</sup> + 20 (EZ-1) <sup>e</sup>	20 (EZ-11) <sup>d</sup>	(E)-16	11	19 (Z)-16
25 <sup>u</sup>	olefin mixture 12(40%), 11(60%)	CF <sub>3</sub> CO <sub>2</sub> H 4% heptane	21	--	10	--	--	82	6 <sup>t</sup>
26	"	"	15	5	2 <sup>s</sup>	6	1	69	17
27 <sup>r</sup>	olefin mixture 12(12%), 11(88%)	"	30	--	4 <sup>s</sup>	12	--	37	45 <sup>t</sup>
28	olefin mixture 12(2%), 11(98%)	"	30		1 <sup>s</sup>	4	1	69	25
29 <sup>f</sup>	olefin 11	CF <sub>3</sub> CO <sub>2</sub> H	21		<1			98	1
30	"	CF <sub>3</sub> CO <sub>2</sub> H 4% heptane	21			10		40	50 <sup>t</sup>
31	products from entry 26	CF <sub>3</sub> CO <sub>2</sub> H 6% heptane	30	1	5 <sup>s</sup>	33	5	7	49
32 <sup>r</sup>	products from entry 28	"	30		2 <sup>s</sup>	28	3	5	61 <sup>t</sup>

<sup>a</sup>Unless noted otherwise, reactions were run at 20 ± 5°C; and GLC analyses were conducted on a BBBT column.

<sup>b</sup>Geometric isomer of 12 with the shorter retention time.

<sup>c</sup>Geometric isomer of 12 with the longer retention time.

<sup>d</sup>Geometric isomer of 20 with the longer retention time.

<sup>e</sup>Geometric isomer of 20 with the shorter retention time.

<sup>f</sup>No spot was detected via AgNO<sub>3</sub>-TLC corresponding to 20 (EZ-1).

<sup>g</sup>No spot was seen via AgNO<sub>3</sub>-TLC corresponding to (Z)-16, so we attribute this peak entirely to 19.

<sup>h</sup>Relative yields do not total 100% because GLC showed one identified peak.

<sup>i</sup>Conducted at 189°C.

<sup>j</sup>We estimate the 12:20 ratio here to be ca. 9:1 from relative intensities of spots on AgNO<sub>3</sub>-TLC.

<sup>k</sup>Both components present in about equal amounts as judged by intensities of TLC spots.

<sup>l</sup>Component 12 predominated, as judged by intensities of TLC spots.

<sup>m</sup>Traces of unidentified components were also produced in this run.

<sup>n</sup>Component 20 predominated, as judged by intensities of TLC spots.

<sup>o</sup>Component 16 (EZ-11) was present only in trace amount.

<sup>p</sup>Largely 20, but might contain some 12 unresolved by GLC (BBBT).

<sup>q</sup>GLC conducted on SE-30, which does not resolve 11 and 20, so this peak might contain some 20.

<sup>r</sup>Relative yields do not total 100% because electronic intensity integration registered small peaks due to circuit noise (or to traces of unknown components), which were disregarded.

<sup>s</sup>Relative proportion of 20 (EZ-1) and 12 (EZ-11) unknown.

<sup>t</sup>Isomer (Z)-16 would not be resolved on GLC (BBBT), but its presence in any significant amount is unlikely in view of virtual absence of its partner (E)-16.

<sup>u</sup>The balance of the material (12.4%) was comprised of trisubstituted olefins 12 and 20, whose individual proportions were not assayed.

dimethyl sulfoxide (DMSO), by phosphorous oxychloride in pyridine, by perchloric acid in hexane, and by perchloric acid in methylene chloride.

The first notable aspect pertains to the run in POCl<sub>3</sub>/Py (entry 5). Double bonds are not likely to migrate under these (alkaline) conditions, and so the product mixture is kinetically controlled. This medium afforded relatively high proportions of olefin with un-

rearranged spirokeleton (16, 39%) and of rearranged olefins with the non-fused bicyclic skeleton (11+12, ca 56%). The dehydration in hot DMSO (entry 4) had a similar outcome and implies that even in this "non-alkaline" medium<sup>13</sup> the olefins produced initially survive as such. These results imply that the non-fused bicyclic skeleton may be the kinetically favored rearranged skeleton even in acid media (entries 1-3, 6-10) where

products can, and do, interconvert. This view is upheld by dehydrations in  $\text{HClO}_4/\text{CH}_2\text{Cl}_2$  monitored as a function of time (entries 7–10). The starting alcohol was consumed entirely with 4.25 hr; and an aliquot worked up at that time and assayed by GLC and TLC showed 23.5% of unrearranged spiroolefins **16** (*E* + *Z*), ca 53% of rearranged olefins (**11** + **12**) with the non-fused bicyclic skeleton, and ca 23% of rearranged olefins with the fused bicyclic skeleton (**19** + **20**). Therefore even within 4.25 hr, this acid medium gave a higher proportion of fused bicyclic products than did the runs in non-acidic media (entries 4 and 5).

As the contact time in the acid medium was increased to 47 hr (entries 7–10), the proportion of fused bicyclic olefins steadily increased to ca 54%, and the non-fused bicyclic products diminished to ca 18%. Although the total proportion of spirocyclic olefins **16** (*E* + *Z*) did not change much during the period (*viz* 23.5% → 32% → 33% → 26%), the ratio of *E/Z*-isomers of **16** steadily diminished from ca 15:1 to ca 2:1. These numbers derive from Table 1 with appropriate adjustments in columns six and ten according to the footnotes. All these results indicate that cation **17** can rearrange to cation **18**, presumably through a reversal pathway via spirocation **15**. To explore the "synthetic" potential of these rearrangements, we studied isomerizations of the alkenes under different conditions (entries 11–32).

*Isomerization of olefins.* Treatment of olefin **11** with  $\text{HClO}_4$  in a homogeneous  $\text{CH}_2\text{Cl}_2$  solution for 4 hr produced a mixture (entry 11) in which the proportion of isomers (**19** and **20**) with the fused bicyclic skeleton was about 10–12%. This proportion steadily increased with time (entries 11 and 15). Qualitatively similar behavior was observed when we shook an olefin mixture rich in **12** (e.g. 97% **12** (*E* + *Z*) plus 3% **11**) in trifluoroacetic acid (TFA) and monitored the changes from 5.75 hr to 23 hr (entries 16–19). The TFA runs were heterogeneous, and we conducted each by shaking sealed ampoules and working them up individually. In these TFA runs we observed traces of spiroalkenes *E*- and *Z*-**16**, but these products did not accumulate. A striking feature of the heterogeneous trifluoroacetic acid isomerization was the substantial proportions of tetrasubstituted olefins **11** and **19** relative to their corresponding trisubstituted isomers **12** and **20**. Specifically, after 23 hr (entry 19), the ratio of **11**:**12** was about 1:2; and the ratio of **19**:**20** was about 3:2. This behavior in heterogeneous medium contrasts sharply with that in homogeneous solution containing a strong acid ( $\text{HClO}_4$ , entries 11–15) or containing a Lewis acid. Thus, pure **19** heated in benzene solution with boron trifluoride etherate (entry 20) was isomerized to a three-component mixture comprised of **20** (*E* + *Z*) and **19** in the ratio 13:1. Similarly, a pure sample of **11** in the same homogeneous medium produced a mixture that strongly favored its trisubstituted isomers **12** (*E* + *Z*) (entry 21). Therefore, with these ring sizes, we have the unfortunate situation of trialkylated alkenes strongly preferred over their tetraalkylated isomers on equilibration in homogeneous medium.<sup>14,15</sup> To overcome this thermodynamic disadvantage in our quest for tetrasubstituted alkene **19**, we focused on isomerizations in heterogeneous medium (TFA). As substrates, we used different mixtures of olefins **11** and **12**, because these two olefins can be conveniently obtained in widely different ratios by appropriate reductive coupling of cyclododecanone.

Entries 22–32, which are representative of many runs we conducted, show that the outcome varies for different

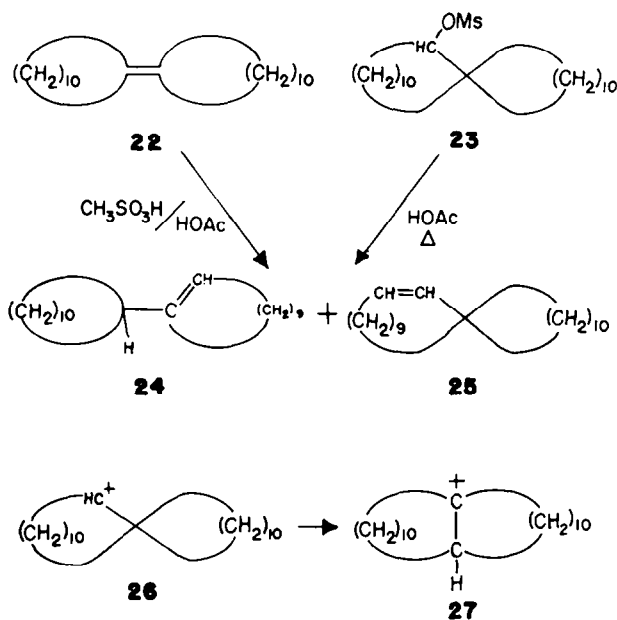
starting mixtures and for different conditions. The Experimental should be consulted for details, but factors that influence the product ratio and, particularly, the proportion of target olefin **19** include: (a) initial ratio of alkenes **11** and **12** and the physical state of this mixture, (b) relative proportions of substrates and TFA, (c) duration of reaction, (d) vigor of agitation of the heterogeneous mixture. Importantly, we discovered that adding a small amount (e.g. 4–6% by volume) of heptane markedly enhances the amount of **19** obtained.

We believe that physical properties (e.g. solubility, crystallinity, size of crystals) of the alkenes play important roles in these heterogeneous isomerizations. For example, the tetrasubstituted isomers **11** and **19** are highly crystalline solids, sparingly soluble in TFA. Trisubstituted alkene **12**, though also not very soluble in TFA, is an oil and presumably can interact more effectively with the TFA when the mixture is shaken. Indeed, a pure sample of crystalline olefin **11** isomerized more slowly than did olefin mixtures rich in oily isomer **12**. The liquid **12** dissolves more readily in heptane than do the solid isomers **11** and **19**, and the beneficial effect of a small amount of heptane (4–6%)<sup>16</sup> may reflect a balance between its solubilizing effect (so the alkenes can become protonated) and the need to avoid true homogeneity (which would allow thermodynamic stability to govern the olefin ratios). In any case, the last ten entries in Table 1 demonstrate that these heterogeneous isomerizations can produce up to 50% of the target *cis*-olefin **19**. Interestingly, in neither our dehydration of spiroalcohol **14a** (entries 1–10) nor our cationic isomerization of alkenes (entries 1–10) nor our cationic isomerization of alkenes (entries 11–32) did we see any product with properties expected for the "trans" isomer of **19**, namely [11, 11]-betweenanene. Nevertheless, we expected this domed isomer ultimately would be available by photoisomerization of **19**.

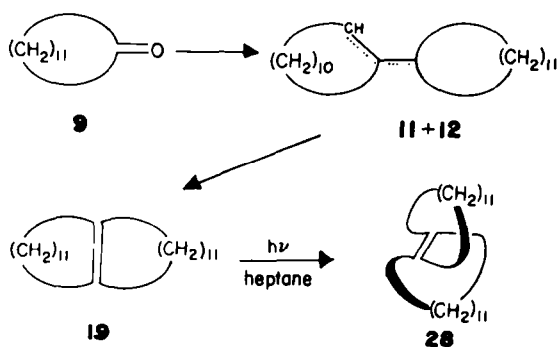
Before proceeding, we should first draw attention to a sharp contrast between our findings on cationic rearrangements of these  $\text{C}_{24}$  substrates and those reported by Marshall *et al.* for analogous  $\text{C}_{22}$  systems.<sup>15</sup> They studied the behavior of olefin **22** in  $\text{CH}_3\text{SO}_3\text{H}/\text{HOAc}$  and also the acetolysis of spirocyclic mesylate **23** (Scheme 3). Olefin **22** gave an 85:15 mixture of isomers **24** and **25**; and mesylate **23** gave a 60:40 mixture of the same two alkenes. (No information about *E-Z* isomerism was provided.) Neither precursor produced any olefins with the fused bicyclic skeleton (corresponding to cation **27**). Marshall *et al.* concluded that ring expansion of spirocation **26** to cation **27** is unfavorable, a situation that clearly is not paralleled in our  $\text{C}_{24}$  series (Table 1). This marked difference in behavior between our  $\text{C}_{24}$  substrates and the reported  $\text{C}_{22}$  analogs is surprising and suggests that predictions for other homologs should not be made; each ring size may require individual examination.<sup>17</sup>

We exploited our findings to effect a 3-step synthesis of [11, 11]-betweenanene **28** via **19** as follows (Scheme 4). Cyclododecanone (**9**) was reductively coupled ( $\text{TiCl}_4/\text{Zn}$ ) to produce, in virtually quantitative yield, a mixture of **11** and **12** in ratios that can differ widely according to the conditions we chose for the coupling (Experimental). This olefin mixture was then isomerized in TFA/heptane, and the desired alkene **19** was isolated by column chromatography. Typically, after recrystallization, we obtained pure **19** in 20–25% overall yields from these two steps.

This olefin, **19**, was then photoisomerized by direct



Scheme 3.



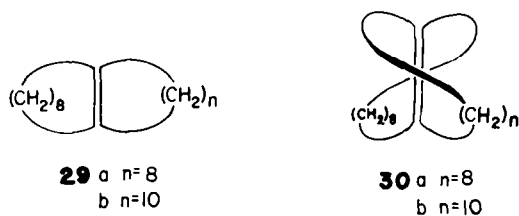
Scheme 4.

irradiation in heptane with a low pressure mercury lamp.<sup>2a,18</sup> Analysis of the crude product revealed starting alkene **19** (37%), a new product (55%) with a shorter retention time, and three minor (8% total) unidentified components. The new product (m.p. 102–103°, 50% yield) had elemental analyses corresponding to  $\text{C}_{24}\text{H}_{44}$ , and we assign to it the “betweenanene” structure **28** based on the following evidence. The proton broad-band decoupled  $^{13}\text{C}$  NMR spectrum of the photoisomer (like those of *cis*-olefin **19** and olefin **11**), indicated a structure of high symmetry. Specifically, it showed only seven signals, including one in the olefinic region ( $\delta$ 134.87).<sup>8</sup> The olefinic C was quaternary according to a single frequency off-resonance decoupling experiment.

The  $^1\text{H}$  NMR spectrum of the photoisomer showed a complex pattern in the allylic region with two separate groups of multiplets ( $\delta$ 1.70–2.08, 4 H, and 2.30–2.70, 4 H). In contrast, the precursor *cis*-olefin **19** shows a single multiplet in the allylic region at  $\delta$ 1.80–2.14. The complexity of the allylic proton signals in the domed isomer **28** reflects the molecular dissymmetry of its structure; the two hydrogens in each allylic methylene are diastereotopic and experience different environments. Nakazaki *et al.* repor-

ted similar  $^1\text{H}$  NMR characteristics for their domed olefins (e.g. **30a** and **30b**).<sup>2a</sup>

The UV spectrum of our photoisomer **28** shows maxima at 212 nm ( $\epsilon = 6700$ ) and 208 nm ( $\epsilon = 6700$ ), and a shoulder at 202 nm ( $\epsilon = 5800$ ). The precursor *cis*-isomer **19** has a single maximum at 200 nm ( $\epsilon = 10,100$ ). The bathochromic shift of up to 12 nm and decrease in molar absorptivity ( $\epsilon$ ) of **28** relative to its *cis*-isomer **19** show that the  $\pi$ -bond is unusual and suggest it may be strained despite the large size of each ring. Nakazaki *et al.* found parallel differences between the UV spectra of domed olefins **30a** and **30b** and their *cis* counterparts **29a** and **29b**.<sup>2a</sup>



Our domed isomer **28** is not adsorbed on  $\text{Ag}^+$  column chromatography, an indication that the  $\pi$ -orbitals are sterically shielded. And, to be sure, we found that **28** was inert to catalytic hydrogenation under conditions that reduced its *cis*-isomer **19** as well as its positional isomer **20**.

In summary, we have shown the viability of a cationic isomerization route by preparing our target domed olefin **28** in only three steps from cyclocodecanone: reductive dimerization to a mixture of alkenes **11** and **12**; heterogeneous treatment of this alkene mixture with trifluoroacetic acid to produce ring fused, *cis* olefin **19**; photoisomerization of **19** to betweenanene **28**. Even though the overall yield in this betweenanene synthesis is only 10–12%, the shortness of our route makes it eminently practicable for this particular case and, per-

haps, for other ring sizes. Cationic rearrangement routes are probably limited to symmetrical betweenanenes, but it may be possible to include heteroatoms at remote sites, with due regard for positional isomerism.

### EXPERIMENTAL

*General.* M.p.s are uncorrected and were taken in Pyrex capillaries on a Thomas-Hoover Unimelt apparatus.

IR spectra were obtained with a Perkin-Elmer Model 457A grating spectrophotometer as solutions in  $\text{CHCl}_3$  or  $\text{CCl}_4$  (0.5 mm Irtran cells, or as neat films or Nujol mulls in NaCl cells. The  $1602\text{ cm}^{-1}$  band of polystyrene film was used as an external calibration standard.

$^1\text{H}$  NMR spectra were obtained at 100 MHz on a JEOL MH-100 spectrometer. Chemical shifts are reported in  $\delta$  units (ppm) downfield from the internal standard TMS.

$^{13}\text{C}$  NMR were obtained on a Varian Model CFT-20 spectrometer (20 MHz) with Fourier transform and with full proton broad-band noise decoupling. Carbon shifts are reported in  $\delta$  units (ppm) downfield from the internal standard TMS. When given, C multiplicities were obtained from separate, single frequency off-resonance decoupling experiments. These spectra were obtained in  $\text{CDCl}_3$  soln except as noted, and the internal D lock was maintained on the solvent.

Elemental microanalyses were performed by Galbraith Laboratories. THF, dioxane, and diethyl ether (ether) were distilled from sodium benzophenone ketyl under  $\text{N}_2$ .  $^{19}\text{BF}_3$ -etherate and pyridine were distilled from  $\text{CaH}_2$ .  $\text{CH}_2\text{Cl}_2$  and hexane were commercial "reagent grade." Heptane was "distilled in glass" spectrophotometric grade.

Molecular Sieves (Mol Sieves) refers to Davison Molecular Sieves Type 4A, Grade 514, 8–12 Mesh.

Brine refers to sat NaCl aq.

The notation TLC refers to analytical TLC on  $7.5 \times 1.5\text{ cm}$  microscope slides coated with Merck silica gel GF-254. The plates were developed with EtOAc/cyclohexane (4/1).

The designation  $\text{AgNO}_3$ -TLC refers to analytical TLC on 250  $\mu$  thick,  $20 \times 5\text{ cm}$  silica gel FG-254 plates with 15%  $\text{AgNO}_3$ , purchased from Analtech. The plates were developed with hexane. Preparative  $\text{AgNO}_3$ -TLC refers to chromatography on  $20 \times 20\text{ cm}$  plates with the same adsorbant 1500  $\mu$  thick, also purchased from Analtech and developed with hexane.

The term GLC refers to analytical studies with a Perkin-Elmer Model 900 gas chromatograph equipped with a flame-ionization detector and a Honeywell Model 16 recorder. Integrations were obtained from triangulation, from a disc integrator, or from a Perkin-Elmer Sigma 10 Chromatography Data Station. Helium carrier gas was used. The columns were 9 ft, 1/8 in. stainless steel, 1.5% SE 30 on Chromosorb W-HMDS 50/100 mesh (SE 30), and 4 ft, 1/8 in. stainless steel, 2.5% BBT<sup>20</sup> on Chromosorb W-HP 100/200 mesh (BBBT). The analyses were performed at 40 psi inlet pressure at a temp of 200 or 210° (SE 30) or at 30 psi inlet pressure at a temp of 190° (BBBT). In describing GLC analyses, we list peaks in order of elution.

The designation  $\text{AgNO}_3$ -silica gel refers to Merck silica gel 60 impregnated with  $\text{AgNO}_3$  as follows so that the adsorbent was 20%  $\text{AgNO}_3$  by weight. A soln of  $\text{AgNO}_3$  (6 g) in distilled water (15 ml) was added to a slurry of silica gel (24 g) in distilled water in a round-bottom flask. Most of the water was evaporated *in vacuo*, then the flask containing the moist silica was kept in an oven (140°) overnight. The resulting free-flowing silica gel was stored in a brown bottle.

1-Cyclododecylcyclohexene (12, E + Z).<sup>6</sup> The reaction was conducted under  $\text{N}_2$  in glassware oven-dried at 140°. A stirred soln of cyclododecanone (Aldrich, 0.912 g, 5.0 mmol) in dry dioxane (30 ml) was chilled in an ice bath while  $\text{TiCl}_4$  (Alfa, distilled once under argon, 1.1 ml, 10 mmol) was added dropwise via syringe. A yellow solid precipitated. (Dioxane- $\text{TiCl}_4$  complex?) Activated  $\text{Zn}^{21}$  (1.3 g, 0.020 mol) was added cautiously in portions. The mixture was heated 20 hr at reflux, the black suspension was cooled to room temp, sat  $\text{Na}_2\text{CO}_3$  aq (6 ml) was added, and the mixture was stirred 0.5 hr. Ether (10 ml) was added and the liquid was decanted from the black sludge, which was washed

repeatedly with ether ( $5 \times 10\text{ ml}$ ). The total organic layer was separated, was washed with water and brine, and was dried ( $\text{MgSO}_4$ ). Evaporation *in vacuo* left a viscous oil (0.880 g), which was chromatographed on a column of Merck silica gel 60 (30 g). Hexane eluted a semi-solid mixture (0.560 g, 67%) of hydrocarbons. Analytical GLC (SE 30 or BBT) showed, in order of elution, 12 (EZ-1) 5%; 12 (EZ-11) 85%; 11 (10%).<sup>7</sup> The assignment of 11 was confirmed by peak enhancement with an authentic sample.<sup>4</sup> The E-Z-isomers of 12 were unresolved on analytical  $\text{AgNO}_3$ -TLC, which showed one minor spot for 11 and one major spot (larger  $R_f$ ) for 12. Preparative  $\text{AgNO}_3$ -TLC gave 12 as an oil shown by GLC to contain the EZ-1 and EZ-11 isomers in a ratio 5:95. The IR and NMR data of this oil supported our structural assignment for 12, but we could not tell unequivocally which peak was E and which was Z.<sup>7</sup> IR ( $\text{CHCl}_3$ ) 2920, 2850, 1460 ( $\text{CH}_2$  scissor)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ 0.90–1.70 (broad envelope, 38 H, ring  $\text{CH}_2$ ), 1.75–2.18 (m, 5 H, allylic protons), 5.05 (t, J = 8 Hz, 1 H, vinylic proton).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ 22.51, 22.62, 22.89, 23.55, 23.75, 23.86, 24.29, 24.63, 24.86, 25.14, 25.29, 26.13, 26.65, 27.57, 29.43, 37.97 (d), 124.48 (d), 143.16 (s). (Found: C, 86.54; H, 13.22.)

Calc for  $\text{C}_{24}\text{H}_{44}$  (332.60): C, 86.66; H, 13.34.

#### 1,1'-Bicyclododecane (10)

(a) From 1-cyclododecylcyclohexene (12) A soln of 12 (0.10 g, 5:95 mixture of geometric isomers) in absolute EtOH (30 ml) with one drop of perchloric acid (70–72%) was shaken 20 hr with  $\text{PtO}_2$  (0.20 g) under  $\text{H}_2$ . The catalyst was filtered off and washed with hexane, and the combined filtrate was washed with  $\text{NaHCO}_3$  aq and brine, was dried with  $\text{MgSO}_4$ , and was evaporated *in vacuo*. The semi-solid residue (0.09 g) showed a single peak on GLC (SE 30 or BBT). Recrystallizations from EtOH, then once from hexane, gave the white analytical sample of 10, m.p. 118.5–119.5°. IR ( $\text{CHCl}_3$ ) 2920, 2855, 1470  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ 1.15–1.70 (broad envelope).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ 33.43 (d), 26.25, 24.13, 23.91, 23.71, 22.92, 22.82. (Found: C, 86.16; H, 14.00) Calc for  $\text{C}_{22}\text{H}_{46}$  (334.61): C, 86.14; H, 13.86.

(b) From cyclododecylidenecyclododecane (11). A soln of 11<sup>4</sup> (0.031 g) in hexane (25 ml) and glacial AcOH (5 ml) was hydrogenated over  $\text{PtO}_2$  (0.1 g) at 45 psig. Workup as in part (a) and purification of the product by column chromatography on Merck silica gel 60 (1 g) and then by recrystallization from hexane gave 10, m.p. 118–119°, identical to the sample from part (a) by  $\text{AgNO}_3$ -TLC, by GLC (SE 30), and by mixture m.p.

*Thermal isomerization of cyclododecylidenecyclododecane (11).* Alkene 11 heated in a sealed, evacuated tube at 230° for 71 hr was converted to a mixture of 11 (96%) and 12 (EZ-11) 4% via GLC (SE 30).

#### Reductive coupling of cyclododecanone to mixtures of 11 and 12. (Large Scale).

Glassware was flame-dried four times under argon. Cyclododecanone (Aldrich) was recrystallized from MeOH; m.p. 60.5–61.5°.

*Run A.* A soln of the ketone (15.0 g, 0.08 mol) in dry dioxane (574 ml) in inert atmosphere was chilled in an ice-salt bath ( $ca -10^\circ$ ) and stirred while  $\text{TiCl}_4$  (Alfa, 18.5 ml, 31.9 g, 0.17 mol) was added dropwise from a syringe. Zn, activated for 3 min as reported<sup>21</sup> (20.9 g, 0.32 mol) was then introduced in virtually one batch through a funnel, and the stirred mixture was heated 21 hr at reflux and then was cooled in an ice bath. Sat  $\text{Na}_2\text{CO}_3$  aq (90 ml) was slowly introduced to the stirred mixture, which was then refluxed 1.5 hr. The hot mixture containing a black sludge was filtered (under vacuum) into a separatory funnel. The sludge, which remained in the flask, was heated and stirred with petroleum ether (e.g.  $8 \times 100\text{ ml}$ ) and heptane (e.g. 350 ml), which were also filtered hot into the separatory funnel. (Olefin 11 sometimes precipitates during the filtration.) The aqueous layer of the filtrate was removed, and the organic layer was washed with brine (150 ml) and was dried with  $\text{MgSO}_4$ . Filtration, and evaporation *in vacuo*, left 12.4 g (93.4%) of white solid containing olefins 12 (EZ-11) and 11 in the ratio 40:60 (BBT 215° 32 psi). Isomer 11 (98% pure, m.p. 154–155°;<sup>4</sup> (lit.<sup>22</sup> m.p. 150–152°) was obtained by one crystallization from heptane.



**Run B.** The reaction was conducted similarly, but the quantities were: ketone (15.0 g, 0.08 mol), dry dioxane (469 ml),  $\text{TiCl}_4$  (17.5 ml, 30.2 g, 0.16 mol), activated zinc (22 g, 0.34 mol). The white solid (13.6, 100%) had **12** (EZ-11): **11** in a ratio of 12:88.

**Run C.** The reaction was conducted similarly, but the quantities were: ketone (15.0 g, 0.08 mol), dry dioxane (472 ml),  $\text{TiCl}_4$  (17.5 ml, 0.16 mol), zinc (22 g, 0.34 mol, activated for ca 10 min). Prior to being washed with brine, the organic layer was filtered through Celite to remove residual white cloudiness. Workup as before left 13.9 g (102%) of a viscous oil containing **12** (EZ-1), **12** (EZ-11), and **11**, in the ratio 5:88:7.

**13-Hydroxyspiro[12.11]tetracosane (14a)** from ketone **13a**.  $\text{LiAlH}_4$  (0.050 g, 1.32 mmol) was added to a soln of known<sup>4</sup> ketone **13a** (0.100 g, 0.25 mmol) in distilled THF (25 ml) under  $\text{N}_2$ . The mixture was refluxed 18 hr, then cooled. It was treated successively with water (50  $\mu\text{l}$ ), 15% NaOH (150  $\mu\text{l}$ ), then water (5  $\mu\text{l}$ ). The resulting suspension was filtered and was washed well with ether. The filtrate was dried (Mol Sieves), then was evaporated *in vacuo*. The crude product was recrystallized from hexane; m.p. 96–99° (77% yield). IR ( $\text{CHCl}_3$ ) 3600 (O–H), 2920, 2840, 1460 (C–H). <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  1.00–1.90 (broad envelope, ring methylenes), 3.40–3.60 (broad, carbonyl proton). <sup>13</sup>C NMR ( $\text{CDCl}_3$ ) 19.27, 20.37, 22.18, 22.44, 22.92, 24.90, 25.44, 25.67, 25.87, 26.28, 26.72, 26.84, 27.26, 27.60, 28.23, 29.09, 30.12, 31.41, 36.22, 42.00, 77.37. (Found: C, 82.01; H, 13.25.) Calc for  $\text{C}_{24}\text{H}_{46}\text{O}$  (350.61): C, 82.21; H, 13.23.

**13-Hydroxyspiro[12.11]tetracosyl 3,5-dinitrobenzoate 14c** from alcohol **14a**. A yellow soln of **14a** (0.120 g, 0.34 mmol) and 3,5-dinitrobenzoyl chloride (0.345 g, 1.70 mmol, 5 equiv) in pyridine (10 ml) was stirred at room temp for 72 hr. It was poured into cold water (50 ml), and the heterogeneous mixture was stirred at room temp for 0.5 hr, then was extracted with ether (4  $\times$  10 ml). The ether was washed successively with water, 3N HCl,  $\text{NaHCO}_3$  aq, and brine, was dried (Mol Sieves) and evaporated *in vacuo*. The yellow oily product (0.167 g) crystallized when scratched and was recrystallized from hexane; off-white solid (0.130 g, 70%), m.p. 121–123°. IR ( $\text{CHCl}_3$ ) 3100, 2920, 2855, 1725 (C=O), 1630, 1600 (aromatic C=C)  $\text{cm}^{-1}$ . <sup>1</sup>H NMR ( $\text{CDCl}_3$ ) 80.90–2.23 (broad envelope, 44 H, methylenes), 5.30–5.50 (multiplet, 1 H, carbonyl H), 9.20 (s, 3 H, aromatic). <sup>13</sup>C NMR ( $\text{CDCl}_3$ ) 162.84, 148.81, 134.44, 129.51, 122.23, 82.58, 42.48, 36.30, 31.68, 29.16, 28.25, 27.46, 26.95, 26.85, 26.18, 25.69, 24.51, 22.88, 22.65, 22.32, 20.93, 20.51, 18.73. (Found: C, 68.42; H, 9.08.) Calc for  $\text{C}_{31}\text{H}_{48}\text{O}_6$  (544.73): C, 68.35; H, 8.88.

**13-Hydroxyspiro[12.11]tetracosyl trifluoroacetate 13d** from alcohol **14a**. Trifluoroacetyl anhydride (Aldrich, 5 ml, 25 mmol) was added to a soln of **14a** (0.200 g, 0.57 mmol) in ether (5 ml), and the soln was allowed to stand at room temp for 70 hr. It was washed successively with  $\text{NaHCO}_3$  aq (until the washings were basic), cold water, cold brine, was dried (Mol Sieves), and evaporated *in vacuo*. The oily residue (0.240 g, 94%) crystallized when triturated with hexane; white solid m.p. 61.5–63.0°. IR ( $\text{CHCl}_3$ ) 2920, 2855, 1772 (C=O), 1155  $\text{cm}^{-1}$ . <sup>1</sup>H NMR ( $\text{CDCl}_3$ ) 80.90–2.00 (broad envelope, 44 H, methylenes), 5.02–5.24 (m, 1 H, carbonyl H). <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  18.65, 19.73, 20.24, 22.14, 22.29, 22.75, 22.91, 24.23, 25.39, 25.52, 25.62, 26.23, 26.45, 26.90, 27.37, 27.75, 28.18, 28.98, 31.42, 36.08, 42.27, 84.90, 114.9 (q,  $J_{\text{CF}} = 286.7$  Hz), 157.8 (q,  $J_{\text{CF}} = 41.6$  Hz). (Found: C, 70.08; H, 9.95.) Calc for  $\text{C}_{26}\text{H}_{44}\text{F}_3\text{O}_2$  (446.64): C, 69.92; H, 10.16.

**15-Hydroxyspiro[14.13]octacosane (14b)**. Alcohol **14b** was prepared from known ketone **13b**<sup>4</sup> according to the procedure described for **14a**. The oily viscous residue after evaporation of the ether crystallized when triturated with hexane (m.p. 99–102°). Recrystallization from MeOH left white solid **14b** (0.082 g, 81%). No m.p. was recorded. IR ( $\text{CHCl}_3$ ) 3360, 3500–3300 (O–H), 2920, 2850 1460 (C–H)  $\text{cm}^{-1}$ . <sup>1</sup>H NMR ( $\text{CDCl}_3$ ) 81.00–1.75 (broad envelope, ring methylenes) 3.32–3.54 (broad, carbonyl proton). (Found: C, 82.44; H, 13.23.) Calc for  $\text{C}_{28}\text{H}_{54}\text{O}$  (406.71): C, 82.68; H, 13.38.

**Reaction of alcohol 14a with trifluoroacetic acid—Brief contact time**

**Isolation of 1-cyclododecylcyclododecene 12 and bicyclo[11.11.0]tetracos-1-ene 20.** A heterogeneous mixture of **14a**

(0.101 g, 0.29 mmol) and trifluoroacetic acid (10 ml) was stirred at room temp. The solid alcohol dissolved, and after a few min a white ppt formed. After 12 min the mixture was poured into ice-cold 10% NaOH aq (100 ml), and was extracted with ether (3  $\times$  10 ml). The combined ether layers were washed with brine, were dried (Mol Sieves), and were evaporated *in vacuo*. The clear oil (0.083 g, 86% yield of hydrocarbons) that remained showed no starting alcohol on TLC. It produced six peaks on GLC (BBBT), and five spots on  $\text{AgNO}_3$ -TLC. The six GLC peaks, listed in order of elution, corresponded to the following alkenes: **12** (EZ-1, 4%), **12** (EZ-11, 53%), **20** (EZ-11, 31%, isolation and characterization described immediately below), (E)-spiroalkene **16** (6%), **11** (4%),<sup>4</sup> tetrasubstituted alkene **19** (2%, isolation and characterization discussed later). The mixture of products was separated by preparative  $\text{AgNO}_3$ -TLC. An oil (0.014 g), isolated from the zone with  $R_f$  0.45–0.60, showed two peaks (6% and 94%) on GLC (BBBT). The oil was identified as **12** (E + Z) by comparison of its <sup>1</sup>H NMR, <sup>13</sup>C NMR, and GLC spectra with those of authentic material.

As additional evidence, we reduced this oil to 1,1'-bicyclododecane (**10**, identified by GLC peak enhancement) by catalytic hydrogenation (Pt, EtOH, hexane, trace  $\text{HClO}_4$ ).

In another run (starting with 0.517 g of alcohol **14a**), a viscous oil (0.028 g) was isolated by preparative  $\text{AgNO}_3$ -TLC from the zone with  $R_f$  0.60–0.70. The oil was identified as **20** (EZ-11) on the basis of the following data: IR ( $\text{CHCl}_3$ ) 2920, 2855, 1460  $\text{cm}^{-1}$ . <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  1.00–1.75 (38 H, m), 1.75–2.40 (5 H, m, allylic H), 5.20 (1 H, broad t,  $J = 7$  Hz). <sup>13</sup>C NMR ( $\text{CDCl}_3$ ) 24.36, 24.50, 24.96, 25.30, 26.04, 26.62, 26.82, 27.09, 27.56, 28.55, 31.36, 34.86, 35.87, 45.71 (d), 125.90 (d), 142.92 (s).

We believe this oil is a single isomer but could not assign its configuration as E or Z. Found: C, 87.10; H, 13.04. Calc for  $\text{C}_{24}\text{H}_{44}$  (332.60): C, 86.66; H, 13.34.

**Reaction of alcohol 14a with trifluoroacetic acid—Prolonged contact time.**

**Isolation of Z-bicyclo[11.11.0]tetracos-1(13)-ene (19).** A heterogeneous mixture of **14a** (0.260 g) and trifluoroacetic acid (20 ml) was stirred magnetically at room temp. The alcohol dissolved, and after a few min a white ppt formed. After 16.5 hr the mixture was a pale brown liquid with clumps of greyish semi-solid. The mixture was worked up as described earlier for the run at brief contact time. The semi-solid product (0.250 g) showed seven peaks on GLC (BBBT) and six spots on  $\text{AgNO}_3$ -TLC. The GLC peaks, listed in order of elution, corresponded to the following compounds: **12** (EZ-1, 2%), **12** (EZ-11, 29%), **20** (EZ-11, 34%), (E)-spiroalkene **16** (7%), olefin **11** (12%), alkene **19** (14%, isolation and characterization described immediately below), unidentified product (2%). The crude product was recrystallized twice from hexane. The resulting white solid (0.027 g) was a mixture of olefin **11** (60%) and alkene **19** (40%) by GLC (BBBT). These two isomers were separated by preparative  $\text{AgNO}_3$ -TLC. Compound **19** was isolated from the faster-moving zone and was recrystallized from hexane to give a white solid, m.p. 129–130°. IR ( $\text{CHCl}_3$ ) 2920, 2850, 1460  $\text{cm}^{-1}$ . <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  1.15–1.65 (m, 36 H), 1.80–2.14 (m, 8 H, allylic H). <sup>13</sup>C NMR ( $\text{CDCl}_3$ ) 23.98, 24.98, 25.61, 26.66, 26.97, 30.56, 133.90 (s). UV (heptane)  $\lambda_{\text{max}}$  200 nm ( $\epsilon = 10,100$ ). (Found: C, 86.76; H, 13.17.) Calc for  $\text{C}_{24}\text{H}_{44}$  (332.60): C, 86.66; H, 13.34.

**Catalytic hydrogenation of alkene 20 (EZ-11).** A soln of **20** (EZ-11, 0.015 g) in heptane (10 ml), EtOH (10 ml), and AcOH (1 ml) was shaken for 17 hr with  $\text{PtO}_2$  (0.060 g) under  $\text{H}_2$  in a Parr hydrogenator. Initially, the  $\text{H}_2$  was 43 psi above atmospheric pressure. The mixture was filtered from catalyst, which was washed with hexane. The filtrate was partitioned between 10% NaOH aq and hexane. The combined organic layers were washed with  $\text{NaHCO}_3$  aq and brine, and were dried (Mol Sieves). Evaporation *in vacuo* left a semi-solid residue (0.028 g). The excess weight indicated some solvent had been converted to non-volatile compounds. These by-products were removed by distillation in a Kugelrohr apparatus at 100–110°/0.5 mm. The pot residue was chromatographed on Merck silica gel 60 (1 g). A white semi-solid (0.009 g) was eluted with hexane. Analysis by

AgNO<sub>3</sub>-TLC showed a single, fast-moving spot with the same R<sub>f</sub> as that of a reference alkane, tetracosane. Although GLC (BBBT) revealed no starting alkene **20**, it showed two new peaks (relative areas 72% and 28%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 80.90–1.75. We believe the two products are *cis*- and *trans*- **21**. Elemental analysis was performed on this mixture. (Found: C, 85.67; H, 14.01.) Calc for C<sub>24</sub>H<sub>46</sub> (334.61): C, 86.14; H, 13.86.

**Catalytic hydrogenation of alkene 19.** Alkene **19** (0.018 g) was reduced by the procedure described above for alkene **20**. The semi-solid product (0.013 g) showed a single, fast-moving spot on AgNO<sub>3</sub>-TLC, and two peaks (relative areas 83% and 17%) by GLC (BBBT). The product alkanes **21** were identical by GLC to those obtained from reduction of **20**.

**Isomerization of alkene 19 with BF<sub>3</sub>·Et<sub>2</sub>O in benzene.** A soln of **19** (0.005 g) in benzene (10 ml) and BF<sub>3</sub>-Et<sub>2</sub>O (0.1 ml) was refluxed for 1.75 hr. The cooled soln was washed with NaHCO<sub>3</sub> aq and brine, and was dried (Mol Sieves). Evaporation *in vacuo* left an oil (0.004 g, 80%) which showed three peaks on GLC (BBBT), and three spots on AgNO<sub>3</sub>-TLC. We identified two of the components as starting **19** (7%) and **20** (EZ-11) (79%). The third component (14%), which had the shortest retention time, was the *E-Z* configurational isomer of **20**, since hydrogenation (Pt, heptane, EtOH, AcOH, 25°, 3 atm) of the mixture gave only two products (76% and 24%) identical by GLC (BBBT) to **21** produced on reduction of pure **19** or pure **20**. This new isomer of **20** is designated *EZ-1* because it has a shorter retention time than the isomer of **20** we isolated from dehydration of **14a**.

**Isomerization of alkene 11 with BF<sub>3</sub>·Et<sub>2</sub>O in benzene.** A soln of **11** (0.33 g) and BF<sub>3</sub>-Et<sub>2</sub>O (0.1 ml) in benzene (10 ml) was refluxed. The reaction was monitored by GLC (SE 30) until there appeared to be no further change (3 hr). The cooled soln was washed successively with NaHCO<sub>3</sub> aq and brine, and was dried (Mol Sieves). Evaporation *in vacuo* left an oil (0.020 g) that consisted (GLC, SE 30) of **12** (*EZ-1*, 5%), **12** (*EZ-11*, 88%), and starting olefin **11** (7%). The SE 30 column was used early in our work before we learned it does not resolve **11** and **20**; so this last peak may have contained some **20**.

**Reaction of alcohol 14a with BF<sub>3</sub>·Et<sub>2</sub>O in CH<sub>2</sub>Cl<sub>2</sub>.** BF<sub>3</sub>-Et<sub>2</sub>O (0.1 ml) was added to a soln of **14a** (0.014 g) in CH<sub>2</sub>Cl<sub>2</sub> (4 ml). After standing at room temp 20 hr, the soln was washed with NaHCO<sub>3</sub> aq and brine, was dried (Mol Sieves), and was evaporated *in vacuo*. The oily product (0.011 g, 82% yield) showed six components on GLC (BBBT) and five spots on AgNO<sub>3</sub>-TLC. The products were identified by comparison with authentic samples: **12** (*EZ-1*, 2%), **12** (*EZ-11*, 40%), **20** (*EZ-11*, 38%), (*E*)-spiroalkene **16** (14%), olefin **11** (1%), and tetrasubstituted alkene **19** (5%).

**Dehydration of alcohol 14a with dimethylsulfoxide.** A soln of **14a** (0.011 g) in dimethylsulfoxide (10 ml) was refluxed 13 hr under N<sub>2</sub>. The soln was cooled and partitioned between water and ether (20 ml). The ether soln was washed with water (three times) and brine (two times), was dried (Mol Sieves) and was evaporated *in vacuo*. Analysis by TLC showed no starting alcohol. The residual oil (strong sulfur-like smell) was chromatographed on Merck silica gel 60 (1 g). The dehydration products (0.007 g, 66% yield) were eluted with hexane. The mixture contained six components by GLC (BBBT); and AgNO<sub>3</sub>-TLC showed five spots. The products were identified by comparison with authentic samples: **12** (*EZ-1*, 4%), **12** (*EZ-11*, 45%), **20** (*EZ-11*, 10%), (*E*)-spiroalkene **16** (35%), olefin **11** (5%), and tetrasubstituted alkene **19** (1%).

The dimethylsulfoxide reaction was repeated on a larger scale (0.070 g of starting, **14a**). (*E*)-spiroalkene **16** (0.014 g, 21%) was isolated by preparative AgNO<sub>3</sub>-TLC.

**Dehydration of alcohol 14a with POCl<sub>3</sub> in pyridine.** A soln of **14a** (0.025 g, 0.07 mmol) in pyridine (10 ml) was treated with distilled POCl<sub>3</sub> (0.1 ml, 1 mmol, 14 equiv). After 7.5 hr at room temp, the mixture was partitioned between water and ether (2 × 20 ml). The combined ether layers were washed with 3N HCl and brine, were dried (Mol Sieves), and were evaporated *in vacuo*. The residual oil (0.018 g, 75%) contained no starting alcohol by TLC. Analysis by GLC (BBBT) revealed five components; and AgNO<sub>3</sub>-TLC showed four spots. The products were identified by comparison with authentic samples: **12** (*EZ-1*,

4%), **12** (*EZ-11*, 41%), **20** (*EZ-11*, 5%), (*E*)-spiroalkene **16** (39%), olefin **11** (11%).

**Attempted reaction of alcohol 14a with *p*-toluenesulfonic acid in CH<sub>2</sub>Cl<sub>2</sub>.** Alcohol **14a** (0.010 g) and *p*-toluenesulfonic acid monohydrate (0.003 g) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (3 ml). After 42 hr at room temp, GLC (SE 30) and TLC showed no reaction had occurred.

**Thermal decomposition of alcohol 14a.** A sample of **14a** sealed in an evacuated mp capillary was heated at 200° for 15 hr. The resulting dark brown oil was examined by GLC (SE 30) but showed no volatile components (i.e. no alkenes, no starting alcohol).

**Attempted reaction of alcohol 14a with perchloric acid in THF.** A soln of **14a** (0.10 g) in distilled THF (5 ml) was treated with perchloric acid (70–72%, 0.1 ml). After 96 hr at room temp, there had been no reaction, as revealed by GLC (SE 30) and TLC.

**Reaction of alcohol 14a with perchloric acid in hexane.** Perchloric acid (70–72%, 0.1 ml) was added to a soln of **14a** (0.010 g) in hexane (5 ml), and the heterogeneous mixture was stirred at room temp. During that time a white ppt formed and then redissolved. After 96 hr, TLC analysis showed no starting alcohol remained. The mixture was washed with NaHCO<sub>3</sub> aq and brine, was dried (Mol Sieves), and was evaporated *in vacuo*. The crude oil (no weight recorded) showed six components by GLC (BBBT), and four spots on AgNO<sub>3</sub>-TLC. The products, listed in order of elution, were identified as follows by comparison with authentic samples: **12** (*EZ-1*, 3%), **12** (*EZ-11*, 72%), **20** (*EZ-11*, 10%), (*E*)-spiroalkene **16** (11%), olefin **11** (3%), and alkene **19** (1%).

**Dehydration of alcohol 14a with perchloric acid in CH<sub>2</sub>Cl<sub>2</sub>.** Perchloric acid (70–72%, 0.5 ml) was added to a soln of **14a** (0.052 g) in CH<sub>2</sub>Cl<sub>2</sub> (25 ml). The heterogeneous mixture was stirred magnetically at room temp and was sampled periodically. Each aliquot was washed with NaHCO<sub>3</sub> aq, then analyzed by AgNO<sub>3</sub>-TLC and GLC (BBBT). All starting alcohol had been consumed by the time the first sample was taken (4.25 hr). The product was entirely alkenes, which were identified by comparison of GLC (BBBT) retention times and AgNO<sub>3</sub>-TLC R<sub>f</sub>'s with those of authentic samples. The products included olefins **12** (*EZ-1*), **12** (*EZ-11*), **20** (*EZ-1*), **20** (*EZ-11*), *F-16*, **11**, **19**, and *Z-16*. The reaction was monitored for 27 hr. During that time, the relative amounts of alkenes **20** (*E* + *Z*) increased. **11** and **12** decreased, and *E-16* increased at first and then decreased. Table 1 summarizes the quantitative aspects of these experiments. We couldn't determine the relative amounts of **19** and *Z-16* because their GLC peaks coincided, but AgNO<sub>3</sub>-TLC revealed both were present in the mixture. Similarly, the GLC peaks of **12** (*EZ-11*) and **20** (*EZ-1*) overlapped. Analysis by AgNO<sub>3</sub>-TLC showed both were present, and **12** predominated.

**Isomerization of alkenes 12 to *cis*-bicyclo[11.11.0]-tetracos-1(13)ene 19 with trifluoroacetic acid.** A semi-solid mixture of **12** (97%) and **11** (3%) prepared by TiCl<sub>4</sub>-Zn coupling of cyclo-dodecanone<sup>4</sup> was placed in each of four 1.5 ml glass ampoules (0.020 g of mixture in each ampoule). Trifluoroacetic acid (1 ml) was added to each ampoule. They were sealed and were shaken vigorously at room temp on a "wrist-action" shaker. After various intervals, the contents were worked up by partition between 10% NaOH aq and heptane. The product mixtures were analyzed by GLC (BBBT) and by AgNO<sub>3</sub>-TLC. No trifluoroacetates were detected by IR. The relative amounts of isomeric alkenes found after each reaction time are shown in Table 1, entries 16–19.

The isomerization reaction was repeated on a preparative scale. A semi-solid mixture (*ca* 90:10) of **12** and **11** (0.205 g) was placed in a glass ampoule (20 ml capacity). Trifluoroacetic acid (10 ml) was added, the ampoule was sealed and was shaken vigorously at room temp 18 hr. The contents were poured into ice-cold NaOH aq. More NaOH aq was added until the mixture was basic. It was extracted with heptane (4 × 25 ml). The combined heptane layers were washed with brine and dried (Mol Sieves). Evaporation *in vacuo* left a white solid (0.200 g). Analysis by GLC (BBBT) showed that the mixture of isomers contained about 30% alkene **19**. The mixture was chromatographed on AgNO<sub>3</sub>-silica gel (10 g). The first 250 ml of hexane eluted a

white solid (0.058 g) which was predominantly **19** by GLC. The solid was recrystallized from hexane to give white needles, m.p. 129–130° (0.043 g, 21% yield). Analysis by GLC showed **19** to be 98% pure. We couldn't remove the unidentified contaminant by further recrystallization from hexane, from EtOH, or from acetone.

**Isomerization of olefin 11 with perchloric acid in CH<sub>2</sub>Cl<sub>2</sub>.** A soln of **11** (0.045 g) in CH<sub>2</sub>Cl<sub>2</sub> (55 ml) was treated with perchloric acid (70–72%, 0.4 ml). The mixture was stirred at room temp and was sampled periodically. Each aliquot was washed well with NaHCO<sub>3</sub> aq, then was analyzed by AgNO<sub>3</sub>-TLC and GLC (BBBT). The reaction was followed for 96 hr. The results are listed in Table 1, entries 11–15.

**Attempted isomerization of non-fused olefin 11 to alkene 19 with trifluoroacetic acid.** Finely-ground crystals of **11** (0.184 g) were placed in a glass ampoule. Trifluoroacetic acid was added (10 ml), the ampoule was sealed, and the heterogeneous mixture was shaken vigorously 21 hr. The contents were partitioned between 30% NaOH aq and heptane. The heptane soln was dried with MgSO<sub>4</sub> and evaporated. The residue (0.181 g) was virtually entirely starting olefin, m.p. 153.7–154.5° (lit.<sup>4</sup> 154–155°), probably a result of its high insolubility in the medium. Only trace amounts of alkenes **12**, **19**, and **20** were present (Table 1, entry 29).

#### **Isomerization of olefin 11 to alkene 19—Effect of heptane.**

A sealed ampoule containing **11** (0.079 g), trifluoroacetic acid (5.0 ml, Aldrich, 99% purity), and heptane (0.2 ml, Burdick and Jackson) was shaken 21 hr at room temp. Workup as described immediately above gave 0.063 g of a mixture containing **11**, **20** (EZ-11), and **19** in the ratio 40:10:50 (Table 1, entry 30), as determined by GLC on BBBT.

#### **Isomerization of mixtures of olefins 12 and 11**

**Starting ratio 12 (93%), 11 (7%).**<sup>23</sup> The mixture (0.067 g) TFA (10 ml), and heptane (0.6 ml) in a stoppered vial were shaken vigorously in a "wrist-action" shaker, at room temp, for 27.5 hr. The contents were added dropwise to a soln of 30% NaOH (18 ml) and heptane (6 ml), with cooling in an ice bath. The vial was rinsed with heptane (20 ml). The combined heptane layer was washed with brine (5 ml), dried over MgSO<sub>4</sub>, concentrated, and analyzed by GLC (BBBT). The results of this run (entry 22) and two related runs that differed in duration and in heptane content are summarized in Table 1 (entries 23 and 24).

**Starting ratio 12 (40%), 11 (60%).** The mixture (0.063 g), TFA (10 ml), and heptane (0.4 ml) was shaken 21 hr at room temp, but the agitation was purposefully kept mild and not vigorous. Workup as before gave a mixture with 6% of **19**. The remainder was starting olefins **11** (82%) and **12** (E + Z, 10%). (See entry 25, Table 1.)

In a large-scale run (mixture 10 g, TFA 633 ml, heptane 24.5 ml), the mixture was vigorously shaken in a stoppered 1000 ml flask for 15 hr. To conserve TFA for possible reuse, the acid layer was drawn off; and the heptane layer was neutralized with 30% NaOH and processed as before. Assay on a BBBT column gave the olefin ratios in entry 26, Table 1.

**Starting ratio 12 (12%), 11 (88%)—Preparative run:** The olefin mixture (5.5 g) was dissolved in hot heptane, and the solvent was evaporated *in vacuo* to leave the solid in a finely divided state. After addition of TFA (350 ml) and heptane (14.6 ml, ca 4 vol %), the stoppered flask was shaken vigorously for 30 hr at room temp. The TFA layer was separated; and alkaline workup of the heptane as before gave 5.25 g (95%) of olefins in ratios (BBBT column) shown in Table 1, entry 27. The product, in petroleum ether, was chromatographed on silica gel (225 g) impregnated with 10% AgNO<sub>3</sub>. Petroleum ether eluted **19**, which gave pure crystals (1.35 g, 24.5%, 99% pure by GLC) after one recrystallization from heptane. Elution with petroleum ether containing 10% benzene initially gave mixtures containing **19**, **11**, and **20** and later gave **11** (1.88 g, 34%), whose purity was 97%.

**Starting ratios 12 (2%), 11 (98%).** The olefin mixture (5.0 g), TFA (318 ml) and heptane (13.3 ml, ca 4 vol %) was vigorously shaken 30 hr. The TFA layer was drawn off, and the heptane layer was neutralized with NaOH as usual. After workup, the white product (4.5 g, 98%) was crystalline and contained the ratios summarized in Table 1, entry 28.

**Repeated isomerizations.** To explore the practicability of using an olefin mixture from one isomerization and recycling it through another isomerization to maximize the production of isomer **19**, we treated the products from entries 26 and 28 each for 30 hr. The usual isomerization procedure in TFA was followed, and the TFA contained ca 6 vol % of heptane. As evident in Table 1 (entries 31 and 32), the proportion of **19** increased; and column chromatography on silica gel –15% AgNO<sub>3</sub> as before led to pure **19** in 20–25% yield based on the olefin quantity prior to the first isomerization.

**Photochemical isomerization of alkene 19 to [11.11]betweenanene (28).** A stirred soln of **19** (0.060 g) in heptane (50 ml) was flushed with N<sub>2</sub> and was irradiated with a low pressure mercury lamp inserted directly into the reaction flask. (Ultraviolet Products Inc., manufacturer of the PCA lamp, reports it emits sharp bands of light at 185 and 254 nm. The quartz envelope of the lamp passes light at 185 nm with 7% of the intensity of the band emitted at 254 nm.) The temp of the soln during irradiation was 35°. No cooling was required. The mixture was sampled hourly, and the samples were analyzed by GLC (BBBT). After 6 hr there was no further change. After 6.5 hr irradiation, the heptane was evaporated *in vacuo*. The white solid residue was shown by GLC (BBBT) to be a mixture of starting **19** (37%), three unidentified minor components (8% total), and a new compound (55%) with a shorter retention time than alkene **19**. Analysis (AgNO<sub>3</sub>-TLC) of the mixture revealed two spots: one corresponded to **19**; the second, faster-moving spot had the R<sub>f</sub> as a reference alkane, tetracosane. This new product was separated from unchanged **19** and from the by-products by chromatography on AgNO<sub>3</sub>-silica gel (3 g). Alkene **28**, a white solid, m.p. 102–103° (0.031, 52% yield), was eluted in the first three hexane fractions (5 ml each). This solid showed a single peak on GLC (BBBT) and a single, fast-moving spot on AgNO<sub>3</sub>-TLC (R<sub>f</sub> corresponding to that of a reference saturated hydrocarbon). One recrystallization from acetone gave the analytical sample (0.021 g), m.p. 103.5–104°. IR (CHCl<sub>3</sub>) 2920, 2850, 1460 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.05–1.70 (m, 36 H), 1.70–2.08 (m, 4 H), 2.30–2.70 (m, 4 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 24.85, 25.12, 25.16, 27.15, 27.73, 30.82, 134.87 (s). UV (heptane) λ max 212 nm (ε = 6700), 208 (ε = 6700), 202 (sh, ε = 5800). (Found: C, 86.62; H, 13.03.) Calc for C<sub>24</sub>H<sub>44</sub> (332.60): C, 86.66; H, 13.34.

**Attempted hydrogenation of [11.11]betweenanene (28).** A soln of **28** (0.020 g, m.p. 103–104°C) in heptane (10 ml) and AcOH (10 ml) was shaken for 20 hr at room temp with PtO<sub>2</sub> (0.150 g) under H<sub>2</sub> in a Parr hydrogenator. The initial H<sub>2</sub> pressure was 43 psi above atmospheric pressure. Workup left a white solid (0.018 g, m.p. 102–103°) which was identical to starting **28** by AgNO<sub>3</sub>-TLC, by GLC (BBBT), and by mixture mp.

**Acknowledgements**—This research was supported by the National Science Foundation, by the National Institutes of Health, and by a Vernon K. Kriebel Fellowship to P.S.J.Z. Messrs. Todd Rose and Abimael Rodriguez provided some valuable laboratory assistance, and Prof. G. Posner gave helpful advice. Specialized spectroscopic assistance and facilities were furnished by Dr. L.-S. Kan and staff at the Johns Hopkins Baltimore Biomedical NMR Center under the auspices of NIH grant GM27512.

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- <sup>6</sup>Modeled on a procedure used for acyclic ketones by T. Mukaiyama, T. Sato and J. Hanna, *Chem. Letters* 1041 (1973).
- <sup>7</sup>To facilitate discussion of geometric isomers of a given olefin,

we use the following terminology: "(E or Z)" signifies an alkene believed to be a single isomer (via GLC), but whose configuration is not assigned. "(E + Z)" signifies a mixture known to contain both isomers; "(EZ-1)" signifies a single isomer, configuration unassigned, and which is eluted earlier on GLC (i.e. shorter retention time) relative to the other member of the pair, designated "EZ-11" and which elutes later on GLC (i.e. has the longer retention time).

<sup>14</sup>J. B. Stothers, *Carbon-13 NMR Spectroscopy*. Academic Press, New York (1972); <sup>15</sup>L. F. Johnson, *Topics in Carbon-13 NMR Spectroscopy*, (Edited by G. C. Levy), pp. 2-16 Wiley, New York (1969).

<sup>16</sup>D. Lenoir, *Synthesis* 553-554 (1979).

<sup>17</sup>This geometric isomer of **20** is labeled EZ-11 because in other experiments (described later) we detected both isomers of **20**; the other isomer has a shorter retention time on GLC and is labeled EZ-1.

<sup>18</sup>For convenience, we use simple cationic intermediates to follow skeletal changes. The actual mechanisms could involve other transient species as well as rearrangements that are concerted with departure of leaving groups and loss of protons.

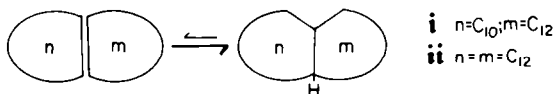
<sup>19</sup>The olefin compositions in Table 1 were determined by GLC. The chromatography column did not resolve olefin **12** (EZ-11) and olefin **20** (EZ-1), and did not resolve olefin **19** and olefin Z-16. These non-resolved pairs are therefore tabulated as such (see columns 6 and 10 in Table 1). However, TLC (AgNO<sub>3</sub>-SiO<sub>2</sub>) does resolve the two components in each pair; and the relative intensity of TLC spots often allowed us to estimate the proportions of the two components (see footnotes to Table 1).

<sup>20</sup>On the issue of alkalinity in dehydrations brought about by DMSO, see: "V. J. Traynelis, W. L. Hergenrother, J. R. Livingston and J. A. Valicenti, *J. Org. Chem.* **27**, 2377 (1962);

<sup>21</sup>P. S. Wharton, C. E. Sundin, D. W. Johnson and H. C. Kluender, *Ibid.* **37**, 34-38 (1972).

<sup>22</sup>Marshall *et al.* have also observed cases where the double bond prefers to be trisubstituted rather than tetrasubstituted in a fused bicyclic skeleton (see i and ii). A monocyclic analog,

1,2-dimethylcyclododecene, also exhibits this atypical characteristic (refs 1 and 15).



<sup>15</sup>J. A. Marshall, T. H. Black and R. L. Shone, *Tetrahedron Letters* 4737 (1979).

<sup>16</sup>Larger amounts of heptane (e.g. 10%) tended to favor trisubstituted isomers and, therefore, disfavored accumulation of the desired tetrasubstituted **19**.

<sup>17</sup>Initially, in our olefin assays, we used a silicon column (SE 30) for GLC. This column did not resolve trisubstituted olefins **12** and **20** and also did not resolve tetrasubstituted olefins **11** and **19**. Only with a column containing a liquid crystal liquid phase (BBBT) were we able to resolve the fused bicyclic alkenes from the alkenes with the non-fused skeleton. In their preliminary publication (ref. 15), Marshall *et al.* did not specify the GLC columns they used.

<sup>18</sup>M. Nakazaki, K. Yamamoto and J. Yanagi, *J. Chem. Soc. Chem. Commun.* 346 (1977).

<sup>19</sup>R. G. Finke and T. N. Sorrell, *Org. Syntheses* **59**, 102 (1979) (see Note 4).

<sup>20</sup>G. M. Janini, G. M. Muschik and W. L. Zielinski Jr., *Anal. Chem.* **48**, 809 (1976).

<sup>21</sup>We prepared activated Zn by stirring commercial Zn dust (50 g. Baker) with 10% HCl (50 ml) for about 3 min. The Zn was filtered and rinsed with distilled water (50 ml) and acetone (50 ml). Slight variations may have occurred in the exact time of exposure of Zn and acid. (See R. Frank and P. Smith, *Org. Synth. Col. Vol.* **111**, 410 (1955).

<sup>22</sup>J. E. McMurry and K. I. Kees, *J. Org. Chem.* **42**, 2655 (1977).

<sup>23</sup>Olefin **12** in this mixture was comprised of E and Z isomers, with a high preponderance of the EZ-11 form, obtained from our reductive coupling of cyclododecanone.