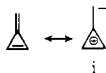


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- (2) For synthetic approaches to the parent hydrocarbon see: (a) T. C. Shields and P. D. Gardner, *J. Am. Chem. Soc.*, **89**, 5425 (1967); (b) I. S. Krull, P. F. D'Angelo, D. R. Arnold, E. Hedaya, and P. O. Schissel, *Tetrahedron Lett.*, 771 (1971).
- (3) The stability of methylenecyclopropene is markedly affected by the introduction of electron-withdrawing groups at the exocyclic position, which result in stabilization of the dipolar form i.



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- (6) **2a**<sup>7</sup> (bp 64–68 °C 0.3 mm) was prepared in 25% yield by addition of dibromocarbene (CHBr<sub>2</sub>, KO-*t*-Bu, pentane, 0–5 °C) to 1,3-di-*tert*-butylallene.<sup>8</sup> Unreacted allene (65%) was also recovered. Spectral data: NMR (CCl<sub>4</sub>) δ 1.14, 1.16 (2 s, 18 H), 2.25 (d, 1 H, J = 3 Hz), and 6.36 (d, 1 H, J = 3 Hz); MS 321.9889 (M<sup>+</sup>), calcd 321.9931.
- (7) The stereochemical assignment of **2a** is made with the expectation that the dibromocarbene would attack from the less hindered side of the allene.
- (8) W. T. Borden and E. J. Corey, *Tetrahedron Lett.*, 313 (1969).
- (9) **2b** was prepared in about 85% yield by treating **2a** with HBr in CCl<sub>4</sub> at 25 °C for 17 h followed by purification by preparative TLC (silica gel, CCl<sub>4</sub>). Spectral data: NMR (CHCl<sub>3</sub>-*d*) δ 1.07 (s, 9 H), 1.27 (s, 9 H), 2.10 (d, 1 H, J = 3 Hz), 5.75 (d, 1 H, J = 3 Hz); MS 321.9891 (M<sup>+</sup>), calcd 321.9931.
- (10) These compounds must be kept in solution at all times.
- (11) The methylenecyclopropenes were added via a direct inlet system in THF at –30 °C. Under these conditions, peaks with masses higher than the parent molecular ion were <0.5% of the base peak (M<sup>+</sup> – Me) and <2% of the parent molecular ion.
- (12) Spectral data: NMR (CCl<sub>4</sub>) δ 1.07 (s, 9 H), 1.30 (s, 9 H), and 2.41 (s, 2 H); ir (neat) 1637 and 1837 cm<sup>-1</sup>; MS 152.1570 (M<sup>+</sup> – CO), calcd 152.1565.
- (13) Spectral data: NMR (CCl<sub>4</sub>) δ 1.05 (s, 9 H), 1.14 (s, 9 H), and 2.21 (s, 2 H); ir (neat) 1687 and 2218 cm<sup>-1</sup>; MS 180.1510 (M<sup>+</sup>), calcd 180.1514.
- (14) We thank Professor Barry Trost for suggesting this catalyst.
- (15) The major product was a nonvolatile oil. Volatile products were separated from the oil by preparative TLC (silica gel, CCl<sub>4</sub>). GC (10% SE-30 on Anakrom ABS, 95 °C) showed five products. Compound **8**, which was purified by preparative GC, accounted for ~75% of the mixture.
- (16) Alfred P. Sloan Foundation Fellow, 1973–1975.
- (17) Note Added in Proof. For the synthesis of other simple methylenecyclopropenes see: P. J. Stang and M. G. Mangum, *J. Am. Chem. Soc.*, **26**, 3854 (1975).

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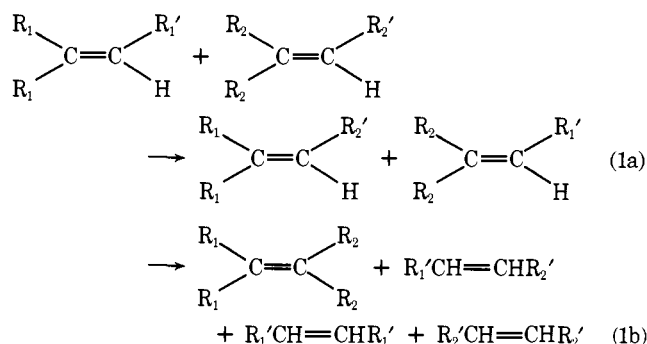
Received July 10, 1975

## Directional Specificity and Stereoselectivity in the Metathesis of a Trisubstituted Olefin

Sir:

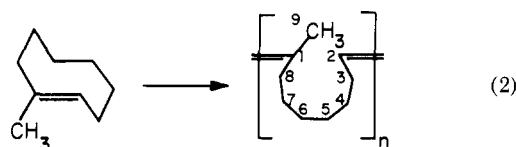
While the metathesis of trisubstituted olefins should give the products in eq 1a rather than those in eq 1b,<sup>1–3</sup> the only indication this is true is the observation that 1-methylcyclobutene gives a polymer that is almost “perfectly alternating”;

it is largely polyisoprene.<sup>1</sup> In this case reaction according to eq 1a outstrips that according to eq 1b by a factor of 10.1 ± 1.2.



While the directional specificity of additions to substituted cyclobutenes is not known, it might be lower than for additions to other cycloalkenes, since alkyl substitution stabilizes carbenium ions less in four-membered rings than in rings of other sizes.<sup>4,5</sup> Accordingly, the directional specificity in metatheses of alkyl cycloalkenes in rings larger than four might be greater. But this is difficult to test because no trisubstituted olefin other than 1-methylcyclobutene has been found to undergo metathesis,<sup>6</sup> although attempts have been made with 1-methylcyclopentene,<sup>1,9,10a</sup> 1-methyl-*cis*-cyclooctene,<sup>9</sup> trimethyl-ethylene,<sup>10b</sup> and *cis*-polyisoprene.<sup>10a</sup>

However, we have found that 1-methyl-*trans*-cyclooctene does undergo the reaction, and it yields a polymer that within the limits of detection of our spectrometer is perfectly alternating (eq 2). Thus to the extent that this reaction is a valid



measure, the selectivity for eq 1a is >50 times that for eq 1b. The experiments also show the stereochemistry of trisubstituted olefin metathesis (*E*-olefins yield mainly *E*-products) and indicate the presence of the metathesis initiator at the ends of the polymer chains.

1-Methyl-*trans*-cyclooctene<sup>11</sup> (≥98% *trans*, 612 mg, 5 mmol) and (diphenylcarbene)pentacarbonyltungsten<sup>12</sup> (122 mg, 0.25 mmol) in an evacuated ampule at 50 °C for 23 h gave a polymer, which was dissolved in CCl<sub>4</sub>, purified by thin layer chromatography (TLC) on silica gel (hexane eluent), and extracted from the origin of the TLC plate by CH<sub>2</sub>Cl<sub>2</sub>. The yield of poly(1-methyl-1-octene-1,8-diyl) was 300 mg (49%). The <sup>13</sup>C nuclear magnetic resonance (<sup>13</sup>C NMR) spectrum (Table I) exhibits 11 peaks of the 18 theoretically distinguishable for *E* and *Z* isomers, but none at ca. 18.2,<sup>1</sup> 36.3,<sup>15</sup> 33.8,<sup>16</sup> or 131<sup>16</sup> ppm, where the head-to-head and tail-to-tail coupling products of eq 1b should have had characteristic resonances. Since such peaks would have been observed if they had been 4% as intense

Table I. <sup>13</sup>C NMR Spectrum of Poly(1-methyl-1-octene-1,8-diyl) in CDCl<sub>3</sub> at 60 °C<sup>b</sup>

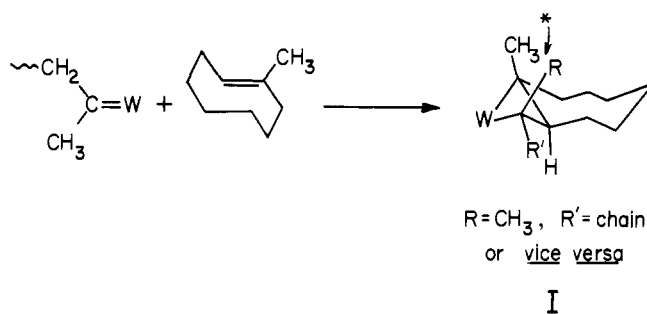
Chemical shift	Assignment <sup>a</sup>	Chemical shift	Assignment <sup>a</sup>
135.32	1Z	29.32	5 and 6 <i>E</i> and Z
135.08	1E	31.86	8Z
125.35	2Z	39.79	8E
124.63	2E	23.39	9Z
28.11	3E and Z	15.92	9E
29.96	4 and 7 <i>E</i> and Z		

<sup>a</sup> Chemical shifts are assigned carbons 1, 2, 3, 8, and 9 by analogy with those in polyisoprenes (ref 13), carbons 4, 5, 6, and 7 by analogy with these in polypentenamers (ref 14), and *cis*-polyheptenamer (unpublished result). <sup>b</sup> Chemical shifts are in parts per million from Me<sub>4</sub>Si.

as a single carbon resonance, reaction 1a occurs at least 50 times as often as reaction 1b.

The percentages of *E* and *Z* isomers, measured by the intensities of the  $^{13}\text{C}$  NMR signals<sup>18</sup> of carbons 2, 8, and 9, was  $76 \pm 1\%$  *E* and  $24 \pm 1\%$  *Z*. This measurement, as well as the structure of the polymer, is confirmed by the proton NMR spectrum, which exhibits five peaks;<sup>20</sup> the intensities of those (at  $\delta$  1.57 and 1.67) assigned to the methyls in the *E* and *Z* isomers<sup>21</sup> are 73:27.

While the directional specificity may be a consequence of carbenium ion stabilization by alkyl substituents, the stereochemical selectivity for forming the *E* stereoisomer may reflect the lesser 1,3-diaxial interaction, indicated in structure I, of a methyl group with another that is unsubstituted,<sup>22</sup>



A significant characteristic of the polymer is its absorption in the ultraviolet spectrum with a maximum at 245 nm. This is where 1,1-diphenyl-1-propene exhibits its ultraviolet absorption maximum ( $\epsilon$  14 000) and the intensities indicate one diphenylethene for every 70 methylcyclooctenes. Since the number average molecular weight measured by gel permeation chromatography is 6800 (the weight av mol wt is 15 500),<sup>23,26</sup> the average chain has, according to these figures, just under one diphenylethene attached to it ( $6800/(70 \times 124) = 0.8$ ). This is one of the best indications that the mechanism of olefin metathesis is a chain reaction in which a metal-carbene is the chain carrier.<sup>2b,27</sup>

Also that, as demonstrated above, an isolable metal-carbene without cocatalysts induces olefin metathesis is in accord with this hypothesis. The generality of this phenomenon is indicated by the discovery that metatheses of disubstituted olefins can be induced similarly by small amounts of (diphenylcarbene)-pentacarbonyltungsten<sup>7,28</sup> and by (phenylmethoxycarbene)-pentacarbonyltungsten.<sup>29</sup>

**Acknowledgment.** We are grateful to Iwao Miura for the NMR spectra.

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- The molecular weights measured assuming the polymer to be polystyrene, the calibration standard, were multiplied by 0.45. This factor was the estimated ratio of the unperturbed dimensions,  $\langle Lo^2 \rangle / M$ , for polystyrene and poly(1-methyl-1-octene-1,8-diyl). The factor was used by analogy with the work of Dawkins et al.<sup>24</sup> The estimate was made assuming  $[\langle Lo^2 \rangle / M]^{1/2}$  to be 0.92 Å for *cis*-polyisoprene and 1.07 Å for polyethylene.<sup>25</sup>
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## New Mechanistic Criterion for Early and Late Transition States

Sir:

Sauer et al.<sup>1</sup> have measured the rates of Diels-Alder reactions of polycyanoolefins as dienophiles. On going from acrylonitrile to tetracyanoethylene (TCNE), one observes a  $4 \times 10^7$ -fold increase of the rate constant towards cyclopentadiene and a  $1.5 \times 10^{10}$ -fold increase vs. 9,10-dimethylantracene (Table I).

We compared the rate constants of 2 + 2 cycloadditions of polycyanoolefins to isobutenyl methyl ether (**1**) with the above-mentioned 4 + 2 cycloadditions. Cyclobutanes **4** were formed virtually quantitatively from 1,1-dicyano-, tricyano-,

