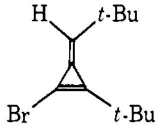
Communications to the Editor

Synthesis of Methylenecyclopropenes

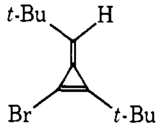
Sir:

Although a number of methylenecyclopropenes with polar substituents on the exocyclic double bond have been reported and some of their chemistry investigated,[1] the parent member[2] or derivatives bearing only alkyl or hydrogen at the exocyclic position,[3] though postulated as intermediates,[4] have not been isolated. We report here the synthesis and some of the properties of a reactive methylenecyclopropene which does not bear a stabilizing polar substituent on the exocyclic double bond.

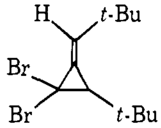
Methylenecyclopropenes **1a** and **1b** were obtained in solution[5,10] when **2a**[6] and **2b**,[9] respectively, were treated with KO-*t*-Bu (3 equiv) in dry THF initially at −60 to −70 °C and then −40 to −30 °C for 1 h. After filtration (−30 °C) under N_2, most of the THF was removed in vacuo at −10 to −20 °C and replaced with CCl_4. NMR and ir spectra were obtained with these solutions at ambient temperature.



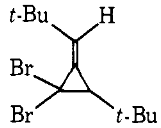
1a



1b



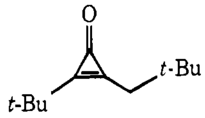
2a



2b

Compound **1a** exhibits NMR singlets at δ 1.05 (*t*-Bu), 1.30 (*t*-Bu), and 3.95 (olefinic), whereas **1b** has singlets at δ 1.03 (*t*-Bu), 1.24 (*t*-Bu), and 4.01 (olefinic). The significantly large upfield shift of the olefinic protons is most likely due to a sizable contribution of dipolar form[3] to the resonance hybrid. Both isomers display a prominent band in the infrared at 1840 cm^{-1}. Elemental composition was provided by high resolution mass spectroscopy: **1a**, 242.0667 (M^+); **1b**, 242.0662 (M^+); calcd 242.0670.[11]

Of particular interest is the extreme reactivity of **1a** and **1b** with water. Thus, when either **2a** or **2b** was treated as described previously with KO-*t*-Bu (1.5 equiv) in THF and allowed to warm to −10 °C, followed by addition of water, two major products identified as the cyclopropenone **3**[12] and the acetylene **4**[13] were isolated by preparative TLC (silicia gel, CH_2Cl_2). **2a** yielded **3** and **4** in 33 and 45% yields, respectively, while the yields from **2b** were 44 and 34%.



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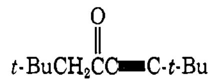
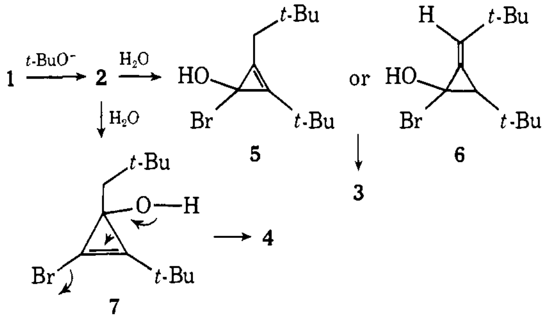


$$t\text{-BuCH}_2\overset{\text{O}}{\overset{\|}{\text{C}}}\text{C}\equiv\text{C-}t\text{-Bu}$$

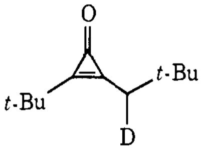
4

Scheme I

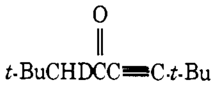


A mechanism for the formation of these products is illustrated in Scheme I. In this scheme, **3** and **4** are rationalized by dehydrobromination of **2** (**a** or **b**) to **1** (**a** or **b**) followed by hydration. Intermediate **5** would result from 1,4-addition of water and would give **3** directly. Formation of **3** via **6** would require double bond isomerization into the ring. **4** probably results from hydration of the polar exocyclic double bond to give **7**, followed by collapse as indicated in the scheme.

Additional evidence for the transformations shown in Scheme I is found in the reaction of **1a** and **1b** with D_2O. Under these conditions **3** and **4** each incorporated one deuterium atom (NMR, mass spectrum), giving **3a** and **4a**. The NMR absorption of **3** at δ 2.41 becomes a 1:1:1 triplet (J = ~2 Hz) for **3a**. Similarly, the singlet of **4** at δ 2.21 becomes a triplet in **4a** (J = ~2 Hz).



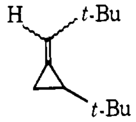
3a



$$t\text{-BuCHD}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{C}\equiv\text{C-}t\text{-Bu}$$

4a

In an attempt to further confirm the carbon skeleton of the methylenecyclopropenes, **1a** was hydrogenated in THF over 5% Rh on alumina.[14] The major volatile product was produced in ~10% yield and identified as **8**.[15] Spectral data: NMR (CCl_4) δ 0.50–1.72 (m, 3 H), 0.89 (s, 9 H), 1.04 (s, 9 H) and 5.49–5.64 (m, 1 H); ir (CCl_4) 1195, 1247, 1363, 1462, and 1474 cm^{-1}; mass spectral 151 ($M^+ - CH_3$). The failure of the exocyclic double bond in **8** to undergo reduction is probably associated with steric protection provided by the *tert*-butyl group.



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We are continuing to investigate the chemistry of these highly reactive molecules and work is now underway on the synthesis of the parent member of the methylenecyclopropene family.[17]

Acknowledgment. We gratefully acknowledge The Robert A. Welch Foundation and Eli Lilly and Company for support of this work.

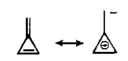
References and Notes

(1) A. S. Kende, *J. Am. Chem. Soc.*, **85**, 1882 (1963); M. A. Battiste, *ibid.*, **86**, 942 (1964); W. M. Jones and J. M. Denham, *ibid.*, **86**, 944 (1964); W. M. Jones and R. S. Pyron, *Tetrahedron Lett.*, 479 (1965); E. D. Bergmann and I. Agranat, *J. Am. Chem. Soc.*, **86**, 3587 (1964); S. Andreades, *ibid.*, **87**, 3941 (1965); B. Föhlisch and P. Bürgle, *Tetrahedron Lett.*, 2661 (1965); T. Eicher and E. Angerer, *Chem. Ber.*, **103**, 339 (1970); S. S. Hecht, *Tetrahedron Lett.*, 4385 (1970); J. W. Lown and K. Matsumoto, *Can. J. Chem.*, **50**, 534 (1972); I. Agranat and M. R. Pick, *Tetrahedron Lett.*, 4079 (1973); / Eicher, T. Pfister, and N. Kruger, *Org. Prep. Proced. Int.*, **1**, 63 (1974); I. Agranat, S. Cohen, E. Aharon-Shalom, and E. D. Bergmann, *Tetrahedron,*

31, 1163 (1975); Review: T. Eicher and J. L. Weber, *Fortschr. Chem. Forsch.*, **57**, 1 (1969).

(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.



i

(4) (a) E. V. Dehmlow, *Chem. Ber.*, **101**, 410 (1968); (b) J. P. Zahra and B. Waegell, *Tetrahedron Lett.*, 2537 (1970); W. E. Billups, T. C. Shields, W. Y. Chow, and N. C. Deno, *J. Org. Chem.*, **37**, 3676 (1972).

(5) Compounds **1a** and **1b** would be expected to derive their stability from steric shielding provided by the *tert*-butyl groups. For similar stabilization of labile systems see: (a) R. L. Camp and F. D. Greene, *J. Am. Chem. Soc.*, **90**, 7349 (1968); (b). J. K. Crandall and W. H. Machleder, *ibid.*, **90**, 7347 (1968); (c) J. F. Pazos and F. D. Green, *ibid.*, **89**, 1030 (1967); (d) G. Maier and A. Alzerreca, *Angew. Chem., Int. Ed. Engl.*, **12**, 1015 (1973).

(6) **2a**[7] (bp 64-68 °C 0.3 mm) was prepared in 25% yield by addition of dibromocarbene ($CHBr_3$, KO-*t*-Bu, pentane, 0-5 °C) to 1,3-di-*tert*-butylallene.[8] Unreacted allene (65%) was also recovered. Spectral data: NMR (CCl_4) 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^+), 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_4 at 25 °C for 17 h followed by purification by preparative TLC (silica gel, CCl_4). Spectral data: NMR ($CHCl_3$-*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^+), 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^+ − Me) and <2% of the parent molecular ion.

(12) Spectral data: NMR (CCl_4) δ 1.07 (s, 9 H), 1.30 (s, 9 H), and 2.41 (s, 2 H); ir (neat) 1637 and 1837 cm^{-1}; MS 152.1570 (M^+ − CO), calcd 152.1565.

(13) Spectral data: NMR (CCl_4) δ 1.05 (s, 9 H), 1.14 (s, 9 H), and 2.21 (s, 2 H); ir (neat) 1687 and 2218 cm^{-1}; MS 180.1510 (M^+), 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_4). 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).

W. E. Billups,[16] A. J. Blakeney
Department of Chemistry, Rice University
Houston, Texas 77001

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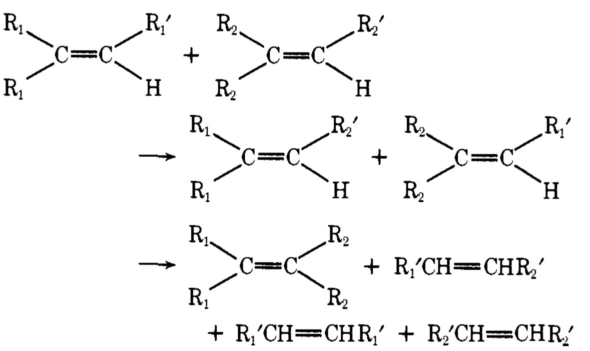
Directional Specificity and Stereoselectivity in the Metathesis of a Trisubstituted Olefin

Sir:

While the metathesis of trisubstituted olefins should give the products in eq 1a rather than those in eq 1b,[1-3] the only indication this is true is the observation that 1-methylcyclobutene gives a polymer that is almost "perfectly alternating"; it is largely polyisoprene.[1] In this case reaction according to eq 1a outstrips that according to eq 1b by a factor of 10.1 ± 1.2.

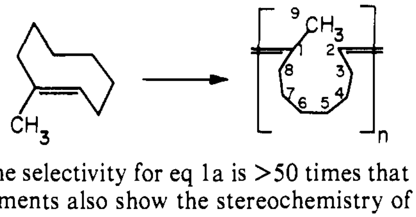


(1a)

(1b)

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.[4,5] 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,[6] although attempts have been made with 1-methylcyclopentene,[1,9,10a] 1-methyl-*cis*-cyclooctene,[9] trimethylethylene,[10b] and *cis*-polyisoprene.[10a]

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.



(2)

1-Methyl-*trans*-cyclooctene[11] (≥98% trans, 612 mg, 5 mmol) and (diphenylcarbene)pentacarbonyltungsten[12] (122 mg, 0.25 mmol) in an evacuated ampule at 50 °C for 23 h gave a polymer, which was dissolved in CCl_4, purified by thin layer chomatography (TLC) on silica gel (hexane eluent), and extracted from the origin of the TLC plate by CH_2Cl_2. The yield of poly(1-methyl-1-octene-1,8-diyl) was 300 mg (49%). The ^{13}C nuclear magnetic resonance (^{13}C NMR) spectrum (Table I) exhibits 11 peaks of the 18 theoretically distinguishable for *E* and *Z* isomers, but none at ca. 18.2,[1] 36.3,[15] 33.8,[16] or 131[16] 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. ^{13}C NMR Spectrum of Poly(1-methyl-1-octene-1,8-diyl) in $CDCl_3$ at 60 °C[b]

Chemical shift	Assignment[a]	Chemical shift	Assignment[a]
135.32	1*Z*	29.32	5 and 6 *E* and *Z*
135.08	1*E*	31.86	8*Z*
125.35	2*Z*	39.79	8*E*
124.63	2*E*	23.39	9*Z*
28.11	3*E* and *Z*	15.92	9*E*
29.96	4 and 7 *E* and *Z*		

[a] 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). [b] Chemical shifts are in parts per million from Me_4Si.