Stereoselectivity in the Cross-metathesis of Oct-1-ene and *cis*- or *trans*-Oct-2-ene

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The yields and the initial ratios of *cis* and *trans* geometries of non-2-ene, tridec-6-ene, or tetradec-7-ene, formed by the cross-metathesis of oct-1-ene and *cis*- or *trans*-oct-2-ene catalyzed by tungsten hexachloride–tetraphenyltin (A), hexaphenoxytungsten–ethylaluminium dichloride (B), or tungsten hexachloride–triethylaluminium (C), have been correlated to the interactions of alkyl substituents on tungstacyclobutane. The results strongly suggest that the 2,4-interaction, between the alkyl substituent on C^2 and the tungsten moiety, plays an important part in determining the distribution of products.

ALTHOUGH several alternative mechanisms have been presented recently,[1,†] it is generally accepted that olefin metathesis proceeds by the chain reaction of a metallocarbene complex with an alkene *via* a metallacyclobutane (Chauvin's mechanism).[2] Chauvin's mechanism affords a sound theoretical ground for the interpretation of the experimental results.

In olefin metathesis, the geometrical isomerism of the reactant alkene is generally retained in the product alkene,[3,‡] and the stereoselectivity is explained by the steric repulsion between the incoming alkene and the ligand on the metallocarbene complex [4] or by the repulsion between the alkyl substituents on the metallacyclobutane.[3-7]

In this paper, the stereoselectivity in the cross-metathesis of oct-1-ene and *cis*- or *trans*-oct-2-ene catalyzed by WCl_6–$SnPh_4$ (A), $W(OPh)_6$–$AlEtCl_2$ (B), or WCl_6–$AlEt_3$ (C) was correlated with repulsions of alkyl substituents on tungstacyclobutane.

RESULTS

The variations of the yields of non-2-ene, tridec-6-ene, and tetradec-7-ene with the reaction time in the cross-metathesis catalyzed by A, B, or C are illustrated in Figures 1—3. The cross-metathesis catalyzed by C proceeded too rapidly to determine the stereoselectivity. When the cross-metathesis was catalyzed by A or B, the following sequence of the initial rates of formation was observed: non-2-ene > tridec-6-ene > tetradec-7-ene.

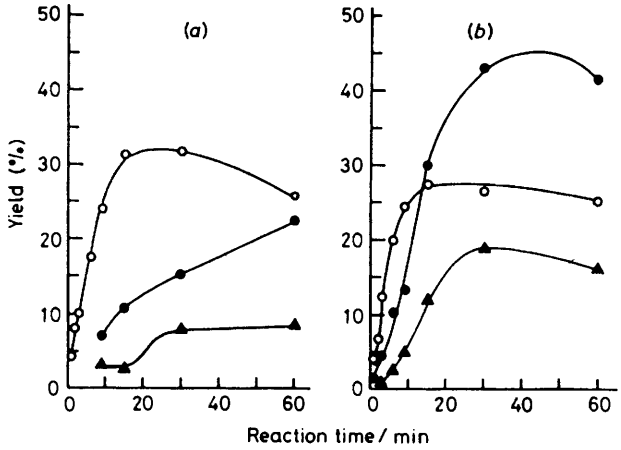


FIGURE 1 Cross-metathesis of oct-1-ene with oct-2-ene catalyzed by A. (*a*) Using *cis*-oct-2-ene; (*b*) using *trans*-oct-2-ene. Products: non-2-ene (○); tridec-6-ene (●); tetradec-7-ene (▲)

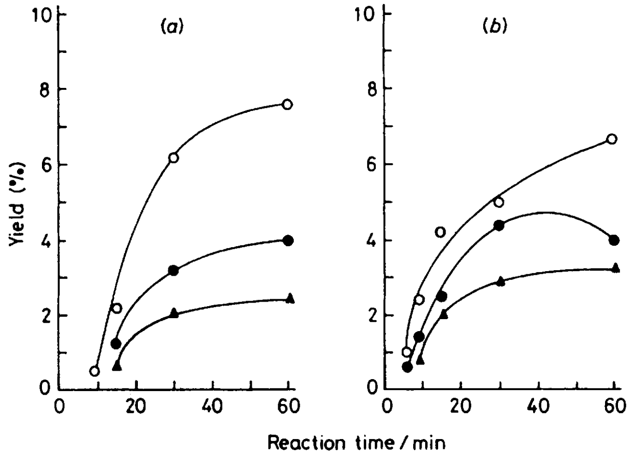


FIGURE 2 Cross-metathesis of oct-1-ene and oct-2-ene catalyzed by B. (*a*) Using *cis*-oct-2-ene; (*b*) using *trans*-oct-2-ene. See Figure 1 for meaning of symbols

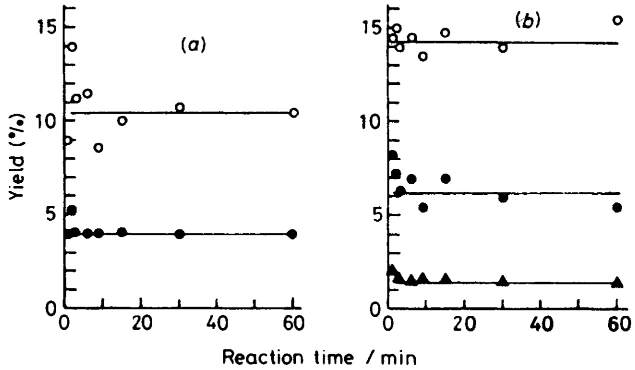


FIGURE 3 Cross-metathesis of oct-1-ene and oct-2-ene catalyzed by C. (*a*) Using *cis*-oct-2-ene; (*b*) using *trans*-oct-2-ene. See Figure 1 for meaning of symbols

The variations of the ratios of *cis* and *trans* alkenes with the yields of corresponding alkenes formed by the cross-metathesis catalyzed by A or B are illustrated in Figures 4

[†] The mechanism *via* a metallacyclobutane, stabilized by a Lewis acid (ref. 1*a*), and the mechanism *via* a dinuclear tungsten complex (ref. 1*b*).

[‡] Olefin metathesis of *cis* alkene gives *trans* alkene in some cases (see ref. 3).

Stereoselectivity in the cross-metathesis catalyzed by A or B

Catalyst *	Co-reactant with oct-1-ene	Initial ratio (*cis*/*trans*) of products		
		non-2-ene	tridec-6-ene	tetradec-7-ene
A	*trans*-oct-2-ene	0.3 : 1	0.3 : 1	0.7 : 1
A	*cis*-oct-2-ene	3.0 : 1	1.4 : 1	0.8 : 1
B	*trans*-oct-2-ene	0 : 1	0 : 1	0 : 1
B	*cis*-oct-2-ene	0 : 1	0 : 1	0 : 1

* A, WCl_6–$SnPh_4$; B, $W(OPh)_6$–$AlEtCl_2$.

and 5. The ratios of *cis* and *trans* alkenes at the initial stages of the reaction were obtained by extrapolating the ratios to zero percentage yield of alkenes and are given in the Table.

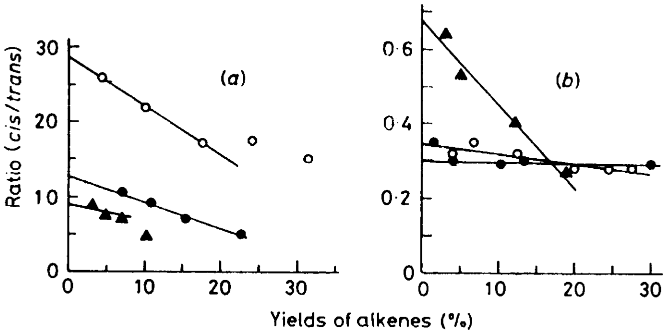


FIGURE 4 Plot of the ratios of *cis* and *trans* geometries of product alkenes against yields of alkenes (catalyst A). (*a*) Reaction of oct-1-ene with *cis*-oct-2-ene; (*b*) with *trans*-oct-2-ene. See Figure 1 for meaning of symbols

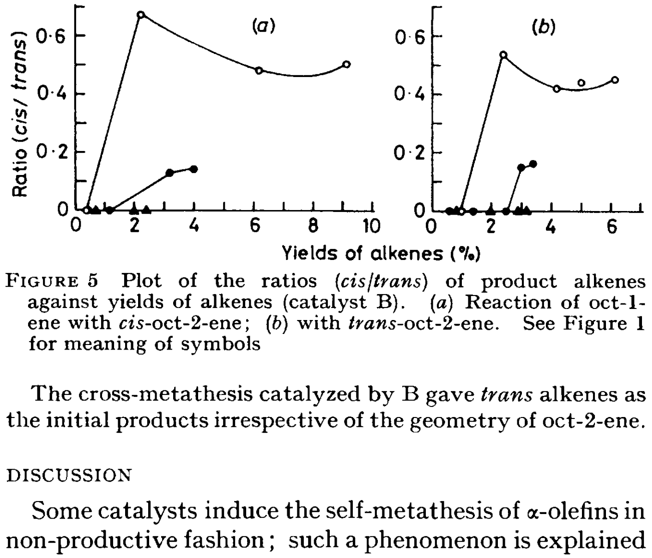


FIGURE 5 Plot of the ratios (*cis*/*trans*) of product alkenes against yields of alkenes (catalyst B). (*a*) Reaction of oct-1-ene with *cis*-oct-2-ene; (*b*) with *trans*-oct-2-ene. See Figure 1 for meaning of symbols

The cross-metathesis catalyzed by B gave *trans* alkenes as the initial products irrespective of the geometry of oct-2-ene.

DISCUSSION

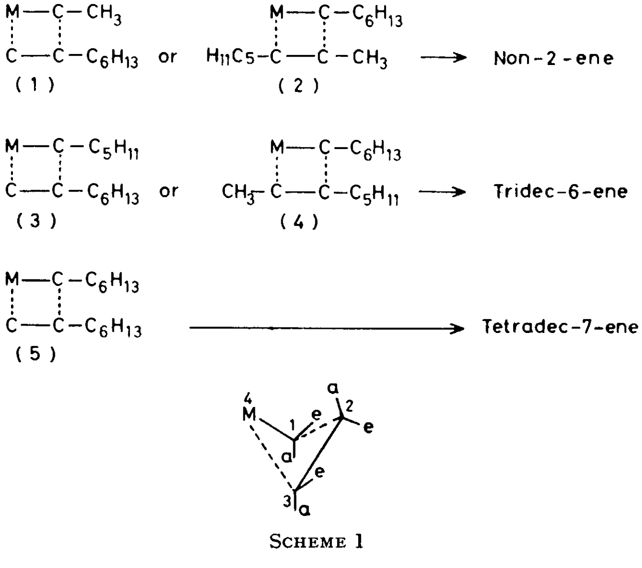
Some catalysts induce the self-metathesis of α-olefins in non-productive fashion; such a phenomenon is explained by the Markownikoff addition of metallocarbene to α-olefin.* In the cross-metathesis of oct-1-ene and oct-2-ene catalyzed by A or B, tetradec-7-ene is formed in similar quantities to non-2-ene or tridec-6-ene; this suggests that the addition of metallocarbene to oct-1-ene is not selective, and that the metallocarbene is not strongly polarized. The cross-metathesis catalyzed by A or B seems, therefore, to be governed by a steric requirement rather than by an electronic factor.

For the formation of non-2-ene, tridec-6-ene, or tetradec-7-ene, the following metallacyclobutanes are required (Scheme 1): (1) and (2) for non-2-ene, (3) and (4) for tridec-6-ene, and (5) for tetradec-7-ene. In the metallacyclobutanes, (1), (3), and (5), the interactions between the two alkyl groups on C^1 and C^2 (1,2-interaction) seem to be in the order, (5) $\geqslant$ (3) > (1).

Since the interactions between the metal and alkyl groups on C^3 (3,4-interaction) were reported to be relatively small,[7] and the 2,3- and 2,4-interactions of (2) are significantly smaller than those of (4), the rates of formation seem to be in the order non-2-ene > tridec-6-ene > tetradec-7-ene.

Because olefin metathesis accompanies the geometrical isomerization of alkenes by non-productive self-metathesis, it is necessary to determine the ratios of *cis* to *trans* alkene at the initial stage of the reaction for a discussion of the effects of the various interactions in metallacyclobutane on the stereoselectivity.

The initial products of the cross-metathesis catalyzed by B are in *trans* geometries irrespective of the geometry of the oct-2-ene; all of the initial ratios (*cis*/*trans*) of the three alkenes are zero. When the cross-metathesis is catalyzed by A, there are linear relationships between the ratios and the yields of corresponding alkenes. The initial ratios (*cis*/*trans*) of the alkenes are determined by extrapolating the ratios to zero percentage yields of alkenes, and are given in the Table. From these initial ratios, the following points become evident. First, the



SCHEME 1

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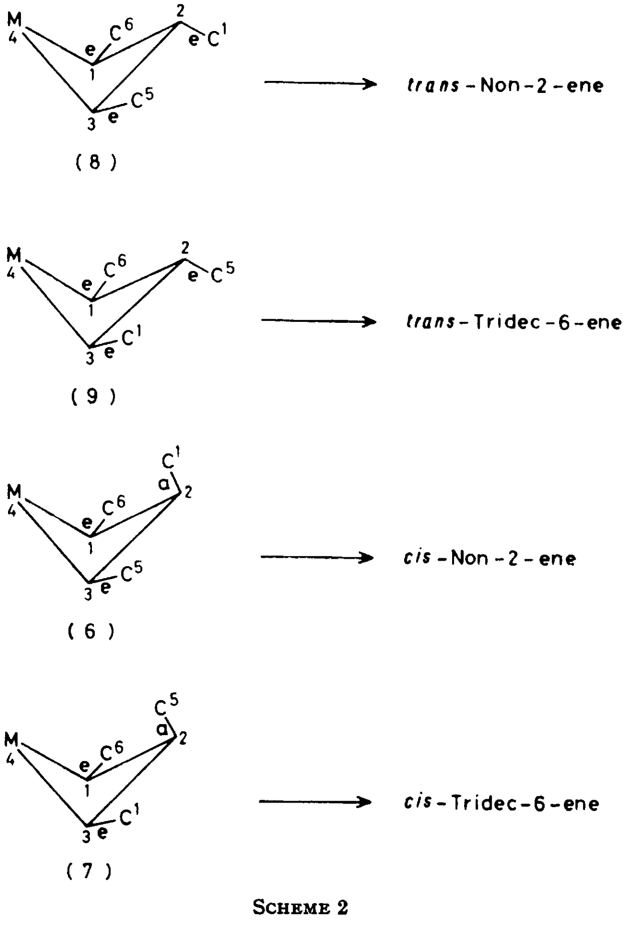
* The non-productive self-metathesis of α-olefin is attributed to the addition of electrophilic carbene-carbon to α-olefin (ref. 5), and to the addition of nucleophilic carbene-carbon to α-olefin (P. G. Gassman and T. H. Johnson, *J. Am. Chem. Soc.*, 1977, **99**, 622).

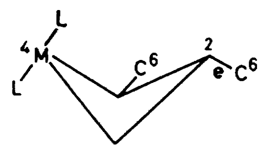
initial ratio (*cis*/*trans*) of tetradec-7-ene is less than 1.0 irrespective of the geometry of oct-2-ene. Secondly, the differences in the initial ratios (*cis*/*trans*) of non-2-ene and tridec-6-ene depend on the geometry of oct-2-ene. Both ratios are almost identical if the co-reactant with oct-1-ene is *trans*-oct-2-ene, while the initial ratio (*cis*/*trans*) of non-2-ene is twice as large as that of tridec-6-ene if the co-reactant is *cis*-oct-2-ene.

The first point is not unexpected because the repulsion of alkyl groups on C^1 and C^2 in (5) leads to the *trans* alkenes. Similarly, (1) and (3) are expected to give *trans* products predominantly. Since *cis*-non-2-ene or *cis*-tridec-6-ene are formed predominantly by the cross-metathesis of oct-1-ene and *cis*-oct-2-ene, the trisubstituted tungstacyclobutanes (2) and (6) should give mainly *cis*-oct-2-ene and *cis*-tridec-6-ene. This suggests that Casey's 1,3-diaxial repulsion [6] is operative in the formation of (6)—(9). The tungstacyclobutanes (6) and (7) are adducts of *cis*-oct-2-ene and a metallocarbene, a metal–heptylidene complex, and are expected to decompose to *cis* alkenes and metallocarbenes. Similarly, the tungstacyclobutanes (8) and (9) correspond to those formed by the addition of *trans*-oct-2-ene to a metallocarbene, metal–heptylidene complex, and should decompose to *trans* alkenes and metallocarbenes (Scheme 2).

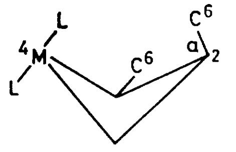
A striking feature of the tungstacyclobutanes, (6) and (7), is the occurrence of 2,4-interactions which are absent in the tungstacyclobutanes, (8) and (9). The second point seems to stem from such interactions.



SCHEME 2



(10)



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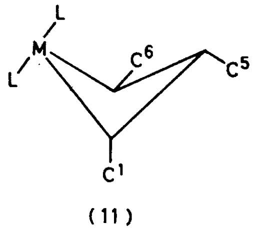

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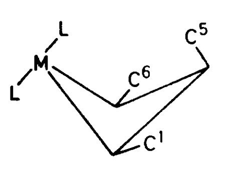

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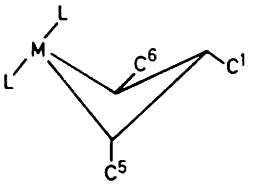

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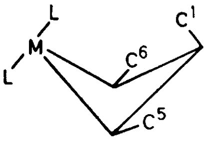

(15)

The cross-metathesis of oct-1-ene and oct-2-ene catalyzed by catalyst B is worthy of note; the products are initially in the *trans* geometry. The tungstacyclobutanes, (10)—(15), are those formed by the addition of oct-1-ene or oct-2-ene to metal–heptylidene complex, and are expected to decompose to non-2-ene, tridec-6-ene, or tetradec-7-ene. When the hexyl group on C^1 of tungstacyclobutanes (10)—(15) is placed in equatorial positions, all of the alkyl groups on C^2 of the tungstacyclobutanes (10)—(12) are in equatorial positions, while those on C^2 of the tungstacyclobutanes (13)—(15) are in axial positions. If the 2,4-interactions become extremely dominant, the formation of *cis* alkenes *via* tungstacyclobutanes (13)—(15) will be prohibited. Although the reason for the predominance of 2,4-interactions for the catalyst B is not clear, the predominant formation of *trans* alkenes by C seems to be caused by this 2,4-interaction.

EXPERIMENTAL

All glassware, including syringes, was flushed with nitrogen. All reactions and manipulations were carried out under nitrogen. Commercial nitrogen of ultra high purity (>99.999%) was used after passing through a column of molecular sieves (5A).

Phenol was distilled before use. Oct-1-ene was distilled and stored over silica gel under nitrogen. The compounds *cis*- and *trans*-oct-2-ene, non-2-ene, tridec-6-ene, and tetradec-7-ene were synthesized from acetylene [8] and stored over sieves under nitrogen. Chlorobenzene was washed with concentrated sulphuric acid and water, dried over phosphorus pentaoxide, distilled, and stored over sieves under nitrogen. The WCl_6 was purified by removing tungsten oxychloride *in vacuo* at 120 °C; $W(OPh)_6$ was prepared from WCl_6 and phenol;[9] and $AlEt_3$ and $AlEtCl_2$ were distilled at atmospheric pressure. n-Decane was washed with concentrated sulphuric acid and water, dried over anhydrous magnesium sulphate, distilled from sodium wire, and stored over silica gel.

A Shimazuseisakusho GC-4B PTF gas chromatograph with a flame ionization detector was used for the vapour pressure chromatography (v.p.c.). The column measured 0.25 mm × 30 m and was coated with Apiezon L grease. n-Decane and nitrogen served as the internal standard and carrier gas respectively, and the temperature of the column bath rose from 50 to 140 °C in 9 min. The peaks of non-2-ene, tridec-6-ene, and tetradec-7-ene were determined by comparison with those of authentic samples. For the measurement of peak areas on the gas chromatograms, an integrator, whose circuit is shown in Figure 6, was used.*

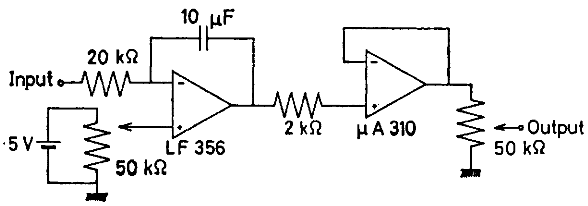

FIGURE 6 Circuit of the integrator used in gas chromatographic measurements; μA 310 and LF 356 are amplifiers

*Cross-metathesis of Oct-*1*-ene and* cis- *or* trans-*Oct-*2*-ene catalyzed by* WCl_6–$SnPh_4$ (A).—After a magnetic stirrer and $SnPh_4$ (0.152 g, 0.355 mmol) had been dried *in vacuo* for 20 min in a Schlenk tube (50 cm^3), WCl_6 (0.0707 g, 0.178 mmol) in chlorobenzene (4.14 cm^3) was added. The mixture was stirred for 5 min at ambient temperature. In another Schlenk tube, oct-1-ene (0.500 g, 4.46 mmol), oct-2-ene (0.500 g), and n-decane (0.69 cm^3) were mixed, and a sample of the mixture (*ca.* 0.001 cm^3) was analyzed by v.p.c. The remainder of the mixture was injected into the incubated catalyst solution. Samples of the reaction mixture (*ca.* 0.1 cm^3) were removed at intervals, and immediately injected into sample tubes containing an aqueous solution of sodium hydroxide (5%). The organic phases in the sample tubes were analyzed by v.p.c. By a similar procedure, the cross-metathesis of oct-1-ene and *trans*-oct-2-ene was carried out.

The variations of yields of non-2-ene, tridec-6-ene, and tetradec-7-ene with reaction time and that of the ratios (*cis*/*trans*) of alkenes with the yields of respective alkenes are illustrated in Figures 1 and 4.

*Cross-metathesis of Oct-*1*-ene and Oct-*2*-ene catalyzed by* $W(OPh)_6$–$AlEtCl_2$ (B).—In a Schlenk tube containing a magnetic stirrer were mixed oct-1-ene (0.500 g), *cis*-oct-2-ene (0.500 g), and n-decane (0.69 cm^3), and a sample of the mixture (*ca.* 0.001 cm^3) was analyzed by v.p.c. A solution of $W(OPh)_6$ (0.133 g, 0.18 mmol) in chlorobenzene (6.4 cm^3) and a solution of $AlEtCl_2$ (0.091 g, 0.72 mmol) in chlorobenzene (0.73 cm^3) were added to the mixture successively, and the reaction mixture was analyzed as previously. By a similar procedure, the cross-metathesis of oct-1-ene and *trans*-oct-2-ene was carried out. The experimental results are illustrated in Figures 2 and 5.

*The Cross-metathesis of Oct-*1*-ene and Oct-*2*-ene catalyzed by* WCl_6–$AlEt_3$ (C).—A sample of a mixture (*ca.* 0.001 cm^3) of oct-1-ene (0.500 g), *cis*-oct-2-ene (0.500 g), and n-decane (0.69 cm^3) was analyzed by v.p.c. A solution of WCl_6 (0.071 g, 0.18 mmol) in chlorobenzene (5.3 cm^3) and a solution of $AlEt_3$ (0.041 g, 0.36 mmol) in chlorobenzene (1.1 cm^3) were added successively to the mixture. The reaction mixture was analyzed as described in the preceding section. The experimental results are illustrated in Figure 3.

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* The output voltage (e_1) on the terminal of the gas chromatograph for the integrator (0—1 mV) is loaded on the input terminal of the integrator: the output voltage of the integrator (e_2) is expressed as follows; $e_2 = (k/RC)\int_t^{t'} e_1 \mathrm{d}t$: G. J. Deboo and C. N. Burrous, ' Integrated Circuits and Semiconductor Devices,' McGraw–Hill Kogakusha Ltd., Tokyo, 1977, p. 128. The output voltage of the integrator is recorded on a recorder and by comparison with the gas chromatogram the peak area can be measured as the differences of the output voltage of the integrator devices at times t and t'.

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