

(19)
(12)(KR)
(A)(51) 。 Int. Cl. ⁷
C07F 1/08(11)
(43)2002 - 0083457
2002 11 02(21) 10 - 2002 - 0022698
(22) 2002 04 25

(30) JP - P - 2001 - 00132016 2001 04 27 (JP)

(71) 가가 가 가
4 5 - 33

(72) 가 2 - 12 - 5

19 - 10 - 1008
가
가 1 - 9 - 1 - 402

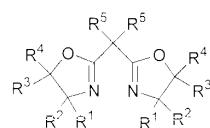
(74)

:

(54)

(a) 1 :

1

[, R¹ R² , , , , , ;]

R^3 R^4 , , , , ,
 R^3 R^4 C_{3-5} ;
 R^5 C_{1-6} ,
 R^5 가 C_{3-6} .];

(b) 1가 2가 ;

(c)

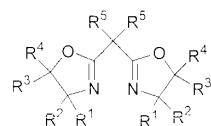
(chrysanthemum - monocarboxylic acid) (+) - 2,2 - - 3 - (2 - - 1 -)
 (pyrethroid) . (+) - 2,2 -

[2 - (4,5 - - 1,3 -)] , ,
 (Tetrahedron Lett., 32, 7373, 1991, etc.). (p
 rochiral)

1.

(a) 1

[1]



[, R¹ R² , , , , ;]

$$\begin{aligned}
 & \mathbf{R}^3 \quad \mathbf{R}^4 \quad , \quad , \quad , \quad , \\
 & \mathbf{R}^3 \quad \mathbf{R}^4 \quad \mathbf{C}_{3-5} \quad ; \quad , \\
 & \mathbf{R}^5 \quad \mathbf{C}_{1-6} \quad , \quad \mathbf{R}^5 \quad \mathbf{J} \quad \mathbf{C}_{3-6} \\
 & .];
 \end{aligned}$$

(b) 1가 2가

(c) ;

(a) 1

(b) 1가 2가 ,

(c) ; ,

$$\mathbb{R}^1 \quad \mathbb{R}^{10} \quad , \quad .$$

- , n- , s- , i- , t- , n- , i- , t- , neo- , n- , s- , i- , n- , n- .

$$\mathbb{R}^5 \times \mathbb{C}_{1-6}, \quad , \quad i =$$

2,2' - [(4R) - 4 - - 5,5 - - (4 -) - 2 -],
 2,2' - [(4R) - 4 - - 5,5 - - (2 -) - 2 -],
 2,2' - [(4R) - 4 - - 5,5 - - (3 -) - 2 -],
 2,2' - [(4R) - 4 - - 5,5 - - (4 -) - 2 -],
 2,2' - [{ (4R) - 4 - - 2 - - 5,1' - }],
 2,2' - [{ (4R) - 4 - - 2 - - 5,1' - }],
 2,2' - [{ (4R) - 4 - - 2 - - 5,1' - }],
 2,2' - [{ (4R) - 4 - - 2 - - 5,1' - }],
 2,2' - [(4R) - 4 - - 2 -],
 2,2' - [(4R) - 4 - - 2 -],
 2,2' - [(4R) - 4 - t - - 2 -],
 2,2' - [(4R) - 4 - - 2 -],
 2,2' - [(4R,5R) - 4 - - 5 - - 2 -],
 2,2' - [(4R,5S) - 4,5 - - 2 -],
 2,2' - [(4R,5S) - 4 - - 5 - - 2 -],
 2,2' - [(4R) - 4 - - 5,5 - - 2 -],
 2,2' - [(4R) - 4 - - 5,5 - - n - - 2 -],
 2,2' - [(4R) - 4 - - 5,5 - - i - - 2 -],
 2,2' - [(4R) - 4 - - 5,5 - - 2 -],
 2,2' - [(4R) - 4 - - 5,5 - - 2 -],
 2,2' - [(4R) - 4 - - 5,5 - - (2 -) - 2 -],
 2,2' - [(4R) - 4 - - 5,5 - - (3 -) - 2 -],
 2,2' - [(4R) - 4 - - 5,5 - - (4 -) - 2 -],
 2,2' - [(4R) - 4 - - 5,5 - - (2 -) - 2 -]

(absolute configuration)

1가 2가 , 1가 2가 ()
1가 2가 .

(Hammett value) " Ho" pK (R.A. Cox, K. Yates, Can. J. Chem., 61, 2225 (1983), .).

, - 10 - 50 " Ho" , 3 pK

, (Nafion,)

()

a), (b) (c) 가 가 , , , ()

1

,

가

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,

1

가

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1

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가

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1

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가
가

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1

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1가

2가

0.9

2

,

1가

2가

0.3

5

,

,

0

60

.

.

,

,

,

,

,

)

)

(packed tower)

,

,

,

2

:

2



$$[\quad , R^6, R^7, R^8 \quad R^9 \quad , \quad \quad \quad ; \quad \quad \quad ;$$

•
,

$$\mathbb{R}^6 \quad \mathbb{R}^7 \quad \mathbb{R}^6 \quad \mathbb{R}^9 \quad , \quad C_{2-4}$$

, R⁶ R⁹ , R⁷ R⁸].

C₂-4

, c_{1-4}) (c_{1-8} .

$$R^6 \quad R^7, \quad \quad R^6 \quad R^9 \quad \quad \quad C_{2-4}$$

4 - - 3 - , 1,1,1 - 2 , , 1 - , , 2 - - 2,5 - - 4 - , 2 - - 2,5 - -
 4 - , 1 - - 2 - - 1 - , 1 - - 2 - - 1 - , 1 - - 2 - - 1 - , 1 -
 - 3 - - 2 - , 1 - - 3 - - 2 - , 1 - - 3 - - 2 - , 1,1 - - 3 - - 2 -
 , 1,1 - - 3 - - 2 - , , - , , - ,

, 2,5 - - 2,4 - , 2 - - 5 - - 2,4 - , 2 - - 5 - - 2,4 -
, 1,1,1 - - 2,5 - - 2,4 - , 1,1 - - 4 - - 1,3 - , 1 - - 1 - - 4 - - 1,3 - , 1,1 -
- 4 - - 1,3 - , 1,1 - - 4 - - 1,3 - , 1 - - 5 - - 2,4 - , 2 -
1 - - 1 - - 4 - - 1,3 - , 2 - - 5 - - 2,4 - , 2 -
- 5 - - 2,4 - , 1 - (,) - 4 - - 1,3 - (conjugated dien

e) . , , 2,5 - - 2,4 -

, 1 , 2 50

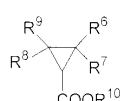
3 : :

$$\text{N}_2\text{CHCO}_2\text{R}^{10}$$

$$[\quad , \mathbb{R}^{10} , \mathbb{C}_{1-8} \quad ; \quad ; \quad ; \quad ; \quad]$$

4

4



$$[\quad , R^6, R^7, R^9 \quad R^{10} \quad]$$

3

(diazotization)

1 2 50 . . . 3 30

0.0002 0.005 , 0.0001 0.01 ,

()
가

, / ,

, 가

4 , ,

2 -

2,2 -

2,2,3 -

2,2 - - 3 - (2,2,2 -) ,

2,2 - - 3 - (2,2,2 -) ,

2,2 - - 3 - (2 - - 2 -) ,

2,2 - - 3 - (2 - - 2 -) ,

2,2 - - 3 - ,

2,2 - - 3 - ,

2,2 - - 3 - ,

2,2 - - 3 - ,

2,2 - - 3 - ,

2,2 - - 3 - ,

2,2 - - 3 - ,

2,2 - - 3 - ,

2,2 - - 3 - (1,3 - - 2 -) ,

2,2 - - 3,3 - ,

2,2 - - 3,3 - ,

4 , ,
2,2 - - 3 - (2 - - 1 -) ,
2,2 - - 3 - (2 - - 1 -) ,
2,2 - - 3 - (2 - - 1 -) ,
2,2 - - 3 - (2 - - 2,2,2 -) ,
2,2 - - 3 - (2,2 - - 1 -) ,
2,2 - - 3 - (2,2 - - 1 -) ,
2,2 - - 3 - (2 - - 2 - - 1 -) ,
2,2 - - 3 - (2 - - 2 - - 1 -) ,
2,2 - - 3 - (2 - - 1 -) ,
2,2 - - 3 - (2 - - 1 -) ,
2,2 - - 3 - (2 - (,) - 1 -) ,
2,2 - - 3 - (2 - - 2 - (,) - 1 -)

가
R¹⁰

가 ,
가 . 가 ,

[1]

$$\text{e.e. \%} = (C - D) \times 100 / (C + D)$$

$$\text{Relative Efficiency} = (E_{\text{new}} - E_{\text{old}}) \times 100 / (E_{\text{new}} + E_{\text{old}})$$

[,

A = ();

B = ();

C = (+) - ;

D = (-) - ;

E = (+) - ;

F = (-) -].

1A

50Mℓ (Schlenk) , 9.8mg(0.022mmol) 2,2'-
 { (4R)-4- - 5,5- - 2- }, 4mg(0.02mmol)
 5Mℓ 가 , 0.5 , 3.0mg(0.02mmol)
 가 , 1 , .

1B

11g(100mmol) 2,5- - 2,4- 1A 가 . ,
 20 10Mℓ(20 30 10mmol) , 2 가 ,
 (chrysanthemate) / GC , , LC
 . 88.4% (), / = 74/26,
 84% e.e. () 24% e.e. () .

1C

1B t - , 1B
 . 1 - , GC
 t - 81.5% (t -), / = 83/17,
 94% e.e. () 60% e.e. () .

2A

1A 가 6.0mg(0.04mmol) , 1A

2B

2A 1B , 1B
 . 1B ,
 % e.e. () 25% e.e. () 89.2% (), / = 74/26, 85

3A

1A

2.8mg(0.02mmol)

1A

3B

3A

1B

1B

90.3% (), / = 74/26, 85
 % e.e. () 33% e.e. ()

4A

1A

4mg(0.04mmol)

1A

4B

4A

1B

1B

87.9% (), / = 72/28, 82
 % e.e. () 29% e.e. ()

5A

1A

2mg(0.02mmol)

2.8mg(0.02mmol)

1A

5B

5A

1B

1B

88.9% (), / = 74/26, 84
 % e.e. () 33% e.e. ()

6A

1A

2mg(0.02mmol)

4.3mg(0.02mmol)

1A

6B

6A

1B

1B

90.7% (), / = 74/26, 85
 % e.e. () 38% e.e. ()

7A

1A

4mg (0.04mmol)
1A

8.6mg (0.04mmol)

7B

7A

1B

, 1B

% e.e. () 93.2% (), / = 75/25, 86
 % e.e. () 40% e.e. () .

8A

1A

2.0mg (0.02mmol)

(cuprous chloride)

1A

8B

8A

1B

, 1B

% e.e. () 88.3% (), / = 74/26, 84
 % e.e. () 25% e.e. () .

9A

1A 2,2' - { (4R) - 4 - - 5,5' - - 2 - } 10.1mg (0.022mmol) 2,
 2' - { (4R,5S) - 4,5' - - 2 - } 1A

9B

9A

1B

, 1B

% e.e. () 84.1% (), / = 73/27, 70
 % e.e. () 35% e.e. () .

10A

9A

53mg (0.1mmol) - ()

10B

10A

†

, 1B

% e.e. () 95.9% (), / = 69/31, 54
 % e.e. () 35% e.e. () .

11A

1A 2,2' - { (4R) - 4 - - 5,5' - - 2 - } 6.5mg (0.022mmol) 2,2' { (4R) - 4 - t - - 2 - } 1A

11B

11A 1.25Mℓ (0.005mmol Cu), 5Mℓ, 3.4g (60mmol),
, 100 - Mℓ 가 . , ,
, 20Mℓ (20mmol) , 2 , 40
, 40 30
GC , 1 - , LC
, 98% () , 96% e.e.
(+)

12A

11A , 1A 2.8mg (0.02mmol)

12B

12A 11B 11B, 98% ()
96% e.e. (+)

13A

50Mℓ , 4mg (0.02mmol)
 5Mℓ 가 , 3.0mg (0.02mmol) 가 ,
 0.5 , 6.5mg (0.022mmol) 2,2' - { (4S) - 4 - t - - 2 - }
 가 1

13B

13A 11B , 11B . 98% (96% e.e. (-)) ,

14A

50Mℓ, 6.5mg(0.022mmol) 2,2'-
 { (4S)-4-t-butyl-2-
 가, 0.5, 4mg(0.02mmol)
 가, 1

14B

14A
96% e.e. (-)

11B
98% (

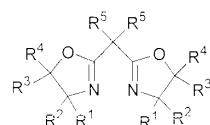
11B
)

(57)

1.

(a) 1

[1]



[, R¹ R² , , , , , ;]

R³ R⁴ , , , , , , ,

R³ R⁴ C₃₋₅ ;

R⁵ C₁₋₆ , , ,

R⁵ 가 C₃₋₆ .];

(b) 1가 2가 ; ,

(c)

2.

1 , 1가 2가 C₂₋₁₅ , , , , , , ,

3.

1 2 , , , , ,
 (Nafion;)

4.

3 , , , , ,
 , , , , ,
 - - - - -

5.

2 , , , ,
 , ,
 .

6.

1 , 1 , 1가 2가 1가 2가 0.3 5 0.9 2
 ,

7.

1

8.

(a) 1 , 1 ;

(b) 1가 2가 ;

(c)

, 1

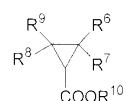
9.

1 , ,
 ,

10.

8 , 4

[4]



[, R^6 , R^7 , R^8 , R^9

; ;

;

, , ,

; ;

, ,

R^6 R^7 R^6 R^9 , C_{2-4} ,

, R^6 R^9 , R^7 R^9 ,

R^{10} ,

C_{1-8} ;

;

;

.]