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ASYMMETRIC CYCLOPROPANATION OF FUMARATES WITH METHYLENE BROMIDE CATALYZED BY COBALT OR NICKEL COMPLEXES

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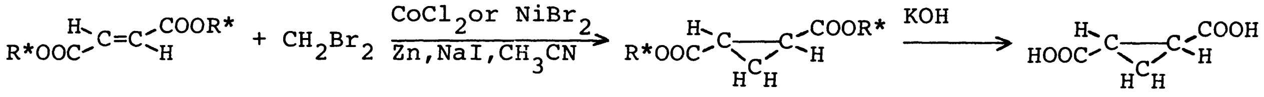
Highly optically active *trans*-1,2-cyclopropanedicarboxylic acid derivatives were prepared from chiral fumarates and methylene bromide catalyzed by cobalt(0) or nickel(0) complexes.

The Simmons-Smith reaction employing chiral olefins and methylene iodide gave lowly optically active cyclopropane derivatives.1) In recent years much interest has been shown in the synthesis of highly optically active cyclopropanes *via* carbenoid reactions with diazo compounds catalyzed by transition metal complexes containing chiral ligands.2),3)

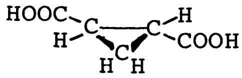
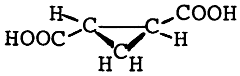
We have found that asymmetric cyclopropanation of chiral fumarates with methylene bromide was carried out by use of cobalt or nickel complexes with chiral substrates themselves as ligands. A mixture of (-)-dimenthyl fumarate((-)-DMFu)(3 mmol), $CoCl_2$ (1 mmol), Zn(8 mmol) and NaI(2.5 mmol) in acetonitrile(10 mmol) was stirred under nitrogen at room temperature for 10 min, during which the color changed from green to red. Methylene bromide(6 mmol) was added and the reaction mixture was stirred for 48 h at room temperature. After hydrolysis of the crude reaction product by 10% KOH solution(EtOH:H_2O = 9:1), (1*R*,2*R*)-*trans*-1,2-cyclopropanedicarboxylic acid was isolated in an 18% yield and a 70% optical yield(O.Y.).



R*= (-)-menthyl, (-)-bornyl, (+)-bornyl

Using (-)-dibornyl fumarate((-)-DBFu), (1*R*,2*R*)acid was obtained in a 40% O.Y., whereas (1*S*,2*S*) acid was produced from (+)-DBFu in almost the same O.Y.(Table 1). Menthyl ester gave higher enantioselectivity than bornyl ester did. Enantioselectivity in cobalt complex system is higher than that in nickel complex one. Optical yield increases with the ratio of (-)-DBFu to cobalt as shown in Fig. 1. At higher concentration of DMFu cobalt species is considerd to be coordinatied by two molecules of DMFu. Ganes et al.4) isolated $Co(fumarate)_2(CH_3CN)_2$ which, in fact, catalyzed cyclopropanation of dimethyl fumarate.5) Another coordination of chiral DMFu may enhance enantioselectivity. The inductive asymmetric cyclopropanation of achiral dimethyl fumarate was carried out to give (1*R*,2*R*)-dimethyl *trans*-1,2-cyclopropanedicarboxylate (2.3% O.Y.)6) in the presence of (-)-DMFu (mole ratio 4:1). The asymmetric cyclopropanation of chiral fumarates is due to the species coordinated on the *re*-face of (-)-chiral olefins or on the *si*-face of (+)-chiral olefins. The

Table 1. Asymmetric cyclopropanation of chiral fumarates with methylene bromide catalyzed by cobalt or nickel complexes.[a]

Fumarate[b]	Catalyst	Yield(%)[c]	Product and Configuration[d]	$[\alpha]_D^{25}$(c, MeOH)	O.Y.(%)[d]
(-)-DMFu	Co	18	 (1*R*,2*R*)	-140°(2.35)	70
	Ni	12		-54°(1.53)	27
(-)-DBFu	Co	12		-78°(1.49)	39
	Ni	9	 (1*S*,2*S*)	+1.2°(1.23)	0.6
(+)-DBFu	Co	55		+94°(5.98)	47

a) Fumarate 3 mmol, CH_2Br_2 6 mmol, $CoCl_2$ or $NiBr_2$ 1 mmol, Zn 8 mmol, NaI 2.5 mmol, CH_3CN 10 ml, r.t. b) Observed specific rotation, (-)-DMFu = (-)-dimenthyl fumarate, $[\alpha]_D^{20}$ = -96.2°(c 1.37 $CHCl_3$); (-)-DBFu = (-)-dibornyl fumarate, $[\alpha]_D^{31}$ = -50.5°(c 4.84 $CHCl_3$); (+)-DBFu = (+)-dibornyl fumarate, $[\alpha]_D^{20}$ = +54.0°(c 1.33 $CHCl_3$). c) Based on fumarates. d) Based on the maximum rotation, -200°; Y, Inoue et al., *Tetrahedron*, 23, 3237 (1967).

asymmetric induction for dimethyl fumarate is due to the chiral metal center originated from the coordination of a chiral olefin. (1*S*,2*S*)-*trans*-1,2-Cyclopropanedicarboxylic acid was obtained in a 6.4% O.Y. in the Simmons-Smith reaction of (-)-DMFu, in which weak interaction between zinc and C=C favors attack of zinc carbenoid onto the *si*-face of the fumarate. The high optical yield in the cyclopropanation by cobalt or nickel complex system is due to the coordination of a chiral substrate and the enhanced chirality of a metal center coordinated by another chiral one.

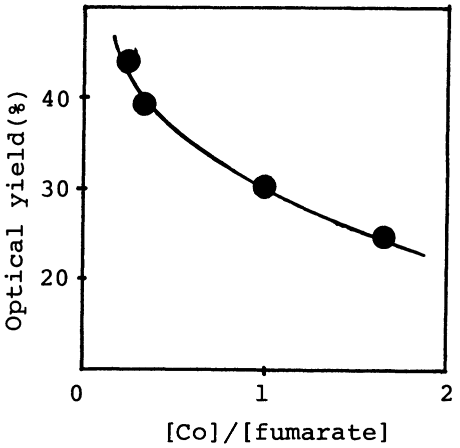


Fig. 1. Effect of the ratio of cobalt to [(-)-DBFu] on the optical yield.

References and Note

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5) H. Matsuda, H. Kanai, N. Hiraki, and Y. Nishiguchi, 46th Symposium on Catalysis(A), Sendai, September 1980, Abstr. No. 60.

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